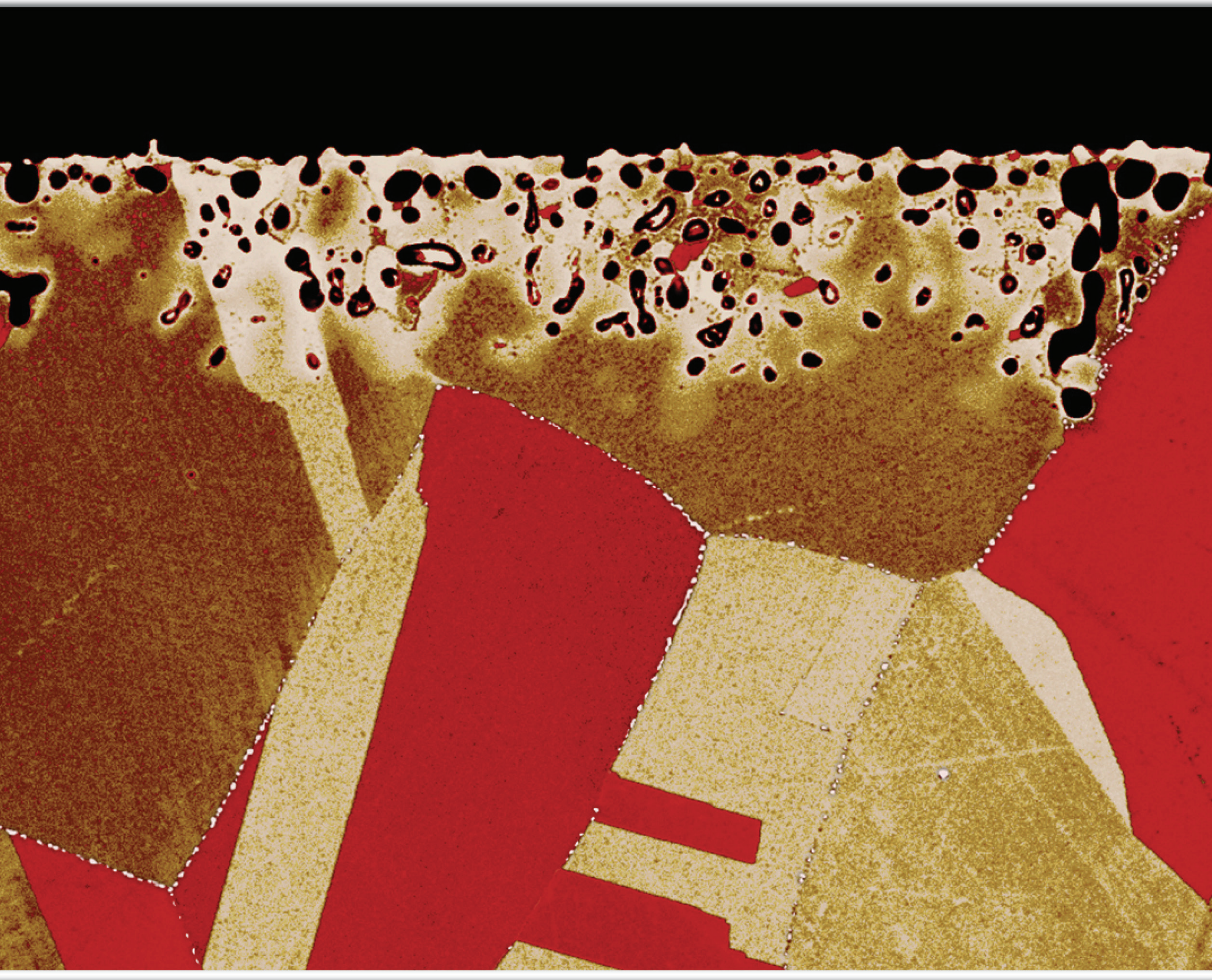
Basic Research Needs for

Future Nuclear Energy



Report of the Basic Energy Sciences Workshop on

Basic Research Needs for Future Nuclear Energy

August 9–11, 2017

The artwork on the cover is a cross-section scanning electron microscope image showing the corroded surface of Inconel 600 alloy after exposure to a mixture of molten salts at 750°C. Scanning electron microscope image courtesy of Donovan Leonard (Oak Ridge National Laboratory).

BASIC RESEARCH NEEDS WORKSHOP FOR
Future Nuclear Energy

REPORT OF THE BASIC ENERGY SCIENCES WORKSHOP FOR FUTURE NUCLEAR ENERGY

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Kelly Beierschmitt (Idaho National Laboratory)

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Michelle Buchanan (Oak Ridge National Laboratory)
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Ian Robertson (University of Wisconsin–Madison)

Panel Leads:
Design and Discovery of Coolants and Liquid Fuels
Phillip Britt (Oak Ridge National Laboratory)
Alexandra Navrotsky (University of California–Davis)

Physics and Chemistry of Interfaces
Amit Misra (University of Michigan)
Jim Wishart (Brookhaven National Laboratory)

Understanding Behavior at Coupled Extremes
Bruce Mincher (Idaho National Laboratory)
Izabela Szlufarska (University of Wisconsin–Madison)

Design and Discovery of Structural Materials and Solid Fuels
Peter Burns (University of Notre Dame)
Pete Tortorelli (Oak Ridge National Laboratory, retired)

Crosscutting Themes
Paul Fenter (Argonne National Laboratory)
Andy Gewirth (University of Illinois, Urbana-Champaign)
Brian Wirth (University of Tennessee–Knoxville)

Technical Coordinator:
Jeremy Busby (Oak Ridge National Laboratory)

Basic Energy Sciences Team:
Linda Horton
Bruce Garrett
John Vetrano
Philip Wilk
Katie Runkles, BES Administrative Lead

Office of Nuclear Energy Team:
Stephen Kung
Sue Lesica

Oak Ridge National Laboratory Publications Team: Brenda Wyatt, Deborah Counce, and Kathy Jones

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ABBREVIATIONS, ACRONYMS, AND INITIALISMS

0D	zero-dimensional
1D	1-dimensional
2D	2-dimensional
3D	3-dimensional
AHTR	Advanced High Temperature Reactor
AIMD	ab initio molecular dynamics
AM	advanced manufacturing
APT	atom probe tomography
ARE	Aircraft Reactor Experiment
bcc	body-centered cubic
BES	Office of Basic Energy Sciences
BESAC	Basic Energy Sciences Advisory Committee
BRN	Basic Research Needs
CVD	chemical vapor deposition
DFT	density functional theory
DOE	Department of Energy
EAC	environment-assisted cracking
fcc	face-centered cubic
GIF	Generation IV International Forum
HBS	high-burnup structure
HF	hydrogen fluoride
IASCC	irradiation-assisted stress corrosion cracking
LWR	light water reactor
MD	molecular dynamics
MGI	Materials Genome Initiative
MSR	molten salt reactor
MSRE	Molten Salt Reactor Experiment
NE	DOE Office of Nuclear Energy

NMR	nuclear magnetic resonance
ORNL	Oak Ridge National Laboratory
PDF	pair distribution function
PRD	Priority Research Direction
SANS	small-angle neutron scattering
SEM	scanning electron microscopy/microscope
STEM	scanning transmission electron microscopy/microscope
TEM	transmission electron microscopy/microscope
UV	ultraviolet
VIS	ultraviolet-visible
VHTR	very-high-temperature reactor
XRD	x-ray diffraction
XRIM	x-ray reflection interface microscopy

EXECUTIVE SUMMARY

Nuclear power today accounts for approximately 20% of the electrical supply for the US. It provides reliable energy that helps to stabilize the national grid. In contrast to current nuclear power facilities, future concepts operate at higher temperatures, are operationally more efficient, more fully utilize the energy stored within the fuel, and reduce the amount of waste produced. Recent advances in chemistry and materials sciences provide an unprecedented opportunity to develop the critical systems—the fuel, coolant, and structural materials—needed for deployment of advanced nuclear reactor designs. To address the challenge of stringent demands on material systems as their properties and performance continuously evolve over the operational lifetime, the frameworks to uncover the underlying processes that cause reduced performance have been developed over the last decade. There is now the prospect of designing materials that report upon their own damage, are self-healing, and leverage what would be considered deleterious chemical processes to increase their performance within advanced reactor designs. Success will provide an energy source needed to secure a stable and safe energy supply for the nation.

To identify the key research directions required to discover the chemical processes and material degradation mechanisms that result in loss of performance of the fuel, coolant, and structural materials, nearly 150 theoreticians, computational experts, and experimentalists from industry, national laboratories, academia, and federal agencies participated in a workshop held in August 2017. Based on the discussions held at the workshop, five Priority Research Directions (PRDs) were identified. These PRDs defined the key scientific challenges that must be met as well as the opportunities that can be exploited to achieve a multi-scale spatial and temporal understanding of fundamental processes that govern the properties and performance of the different material systems required for advanced reactors.

This report recognizes that the requirements needed to realize future nuclear energy systems present a daunting challenge for the chemical and materials sciences. Recent advances in modeling and simulation, data analytics, synthesis and processing science, and in situ characterization capabilities are discussed as an unparalleled opportunity: it is now possible to uncover the fundamental science governing the chemical processes and material responses that result in the degradation in properties and loss of performance of the fuel, coolant, and structural materials. The report concludes that the knowledge resulting from the PRDs defined during the workshop will enable the design, discovery, and production of revolutionary materials, coolants, and fuels required for operation in complex, evolving, harsh environments. The challenges and opportunities outlined will build the scientific basis required to further the development of a new generation of nuclear energy sources to meet the future energy needs of the nation for the next century.

Priority Research Directions for Future Nuclear Energy

Enable design of revolutionary molten salt coolants and liquid fuels. *Key question: How can we characterize and predict the structure, dynamics, and energetics of molten salts— including an evolving chemical composition across length and time scales?* For many future reactor concepts, molten salt coolants and liquid fuels are key elements. During reactor operation, these materials exhibit a heterogeneous and evolving chemical composition, leading to large variations in structure, dynamics, and thermodynamics over broad time and length scales. Elucidating the changes in chemical composition, as well as the impact of these changes on physical and chemical properties, is necessary to optimize their designs. Attaining understanding will require new approaches to understand phase evolution and thermodynamics, including the use of model systems to benchmark computational models, theories, and instrumentation.

Master the hierarchy of materials design and synthesis for complex, reactor environments. *Key question: How do we design, synthesize, and process superior materials able to function and perform* *over decades in the extreme environments of advanced nuclear reactors?* The infrastructure for nuclear energy consists of solid materials. The application of computational methods coupled with innovative synthesis and processing tools will permit tailoring both the composition and structure of solid fuels and structural materials for targeted functionality. This capability will foster precise creation of specific materials for experiments to probe the underlying physical and chemical processes and mechanisms responsible for the degradation of materials exposed to extreme radiation, heat, stress, and chemical reactivity.

Tailor interfaces to control the impact of nuclear environments. *Key question: How can the multitude of inextricably linked chemical and physical processes that occur at interfaces be controlled?* Interfaces between materials and phases dominate the infrastructure of energy production—from structural components exposed to liquid coolants, to the interior microstructures of constituent materials. Interfaces in future nuclear systems—both fluid/solid and solid/solid—will be exposed to a wide variety of extreme and evolving conditions that can lead to degradation of materials and eventual failures. The complex networks of processes that occur at these interfaces need to be understood and controlled to ensure long-term performance and reliability.

Reveal multiscale evolution of spatial and temporal processes for coupled extreme environments. *Key question: How can computational and experimental techniques be integrated to bridge spatial, temporal, and energy scales that underpin materials' behavior and chemical transformations in coupled extreme environments?* Many mechanical and chemical processes can occur separately or in combination over a wide range of time and length scales, acting to degrade materials subjected to the extremes envisioned for future reactor systems. Integration of experimental and computational capabilities is required to reveal the complex networks of processes and mechanisms that evolve over such broad temporal and spatial scales. This critical knowledge is required to inform the design of a new generation of materials and predict their long-term behavior and performance.

Identify and control unexpected behaviors from rare events and cascading processes. *Key question: How do we identify, anticipate, and control rare events that initiate cascading processes and cause aberrant properties and materials' responses?* In the extreme conditions found in nuclear energy environments, high-impact, low-frequency events can change the properties of materials in ways that could ultimately lead to unexpected behaviors and potentially catastrophic failures. Variability in materials, impurity-controlled reactivity, sensitivity to radiation/radiolysis, localized transient behavior, and chemical evolution can act separately or synergistically to trigger a critical event and launch a cascade of unforeseen events. Scientific understanding of these conditions is central to the design of future nuclear energy systems.

1. INTRODUCTION

Nuclear energy is a critical component of the US energy portfolio, reliably producing energy around-the-clock and complementing electricity generation from combustion of fossil fuels and from renewable sources such as solar and wind. Today, the United States has 99 operating nuclear power plants, largely based on a water-cooled reactor design, that supply approximately 20% of the nation's electricity (https://www.eia.gov/energyexplained). The future of nuclear energy requires new concepts to move beyond the water-cooled designs of the previous century to achieve improved efficiency, greater fuel utilization, reduced high-level waste generation, and enhanced safety.

Meeting these requirements necessitates developing entirely different concepts for reactor systems comprising coolants, fuels, and structural materials that can last through decades- to centuries-long reactor lifetimes and withstand some of the most extreme environments known—operational temperatures approaching 1000°C, intense radiation fields, and corrosive environments, among others. These conditions far exceed those of the current operating reactor fleet, requiring revolutionary advances in chemistry and materials science to realize the full potential of future nuclear energy systems. These advances will be achieved only by addressing gaps in our understanding of fundamental chemical and physical processes projected to occur under the extreme conditions encountered in future nuclear systems, and by using this knowledge to design a new generation of materials and chemical systems.

The Office of Basic Energy Sciences (BES) within the Department of Energy (DOE) Office of Science convened a workshop August 9–11, 2017, charged with identifying fundamental research priorities in chemistry and materials science needed to address these knowledge gaps. With this focus, the workshop was intended to go well beyond the topics covered by the 2006 Basic Research Needs workshop report on Advanced Nuclear Energy Systems and the 2007 Basic Research Needs workshop report on Materials under Extreme Environments, taking full advantage of the array of advances that have been realized in materials and chemistry—including characterization and computational techniques and tools—over the intervening decade. Before the workshop, BES worked closely with the DOE Office of Nuclear Energy (NE) to define future requirements for nuclear energy from the perspective of fuels, materials, and other areas relevant to future reactor concepts. In addition, leaders in nuclear energy from universities, industry, and national laboratories partnered to prepare a factual status document (posted separately with this report at https://science.energy.gov/bes/community-resources/reports/), which provided a reference for the workshop attendees and served as a foundation for the discussions.

The workshop included approximately 80 participants and 60 invited observers, representing universities, national laboratories, industry, and DOE offices (Appendices A and B). A plenary session opened the workshop with five presentations focused on key challenges and opportunities for future reactor concepts. The presentations emphasized the enormity of the challenges—understanding myriad physical and chemical processes across scales ranging from femtoseconds to decades and from angstroms to meters. Workshop participants were divided into four technical panels for in-depth discussions:

1. Design and Discovery of Coolants and Liquid Fuels
2. Physics and Chemistry of Interfaces
3. Understanding Behavior at Coupled Extremes
4. Design and Discovery of Structural Materials and Solid Fuels

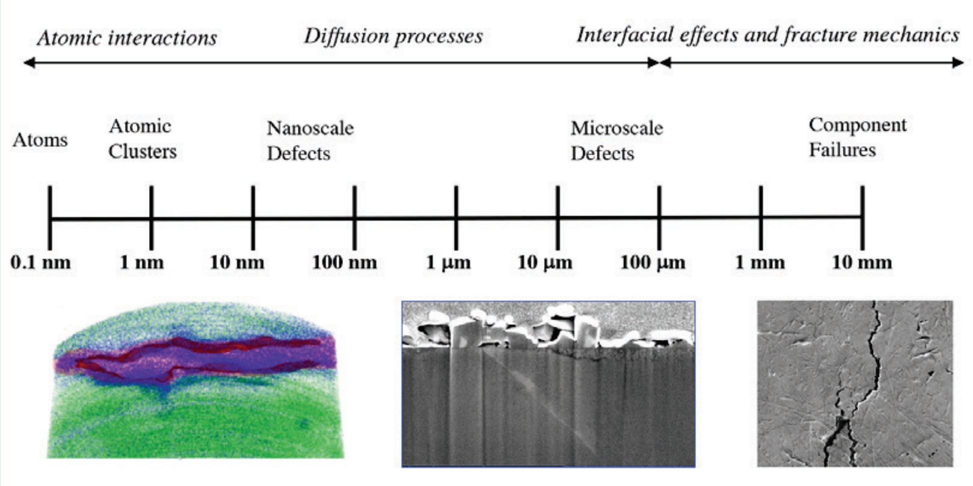
A fifth panel considered research opportunities that cut across the four panel areas. These panels were charged with defining Priority Research Directions (PRDs) that are critical to address the challenges for future nuclear energy technologies.

From these panel discussions, five PRDs were identified:

1. Enable design of revolutionary molten salt coolants and liquid fuels
2. Master the hierarchy of materials design and synthesis for complex, reactor environments
3. Tailor interfaces to control the impact of nuclear environments
4. Reveal multiscale evolution of spatial and temporal processes for coupled extreme environments
5. Identify and control unexpected behaviors from rare events and cascading processes

These PRDs, discussed in depth in the next chapter of the report, define the key scientific challenges that must be met, as well as the opportunities that can be exploited, to achieve a multiscale spatial and temporal understanding of fundamental processes that govern the properties and performance of the different material systems required to function in advanced reactors. The remainder of the report is devoted to summaries of the broader panel discussions. These summaries provide additional context and background relevant to the community's endeavors to advance this critical research. The challenges and opportunities outlined in this report provide the scientific base for innovation in materials systems and chemical processes required for nuclear energy sources that will safely and economically meet future energy needs.

Designing Materials for the Extreme Reactor Environment



Images courtesy of Oak Ridge National Laboratory, Pacific Northwest National Laboratory, and University of Michigan

Physical and chemical processes in extreme environments—including corrosion, oxidation, cracking, and fatigue—span broad length and time scales from atoms (left) to components (right), which can result in degradation of desired properties and, ultimately, failures.

Materials in nuclear reactors are exposed to some of the highest extremes in temperature, pressure, radiation, chemical reactivity, stress, and strain; and they must be designed to withstand these extremes for decades. Understanding and mitigating the mechanisms responsible for degradation are critical to meet the challenges for future nuclear reactors. Achieving this understanding requires information gleaned from experiments and modeling—from the atomic scale, to explain how atoms and molecules are arranged and may evolve, all the way to the mesoscale, to elucidate effects that result in macroscopic changes.

2. PRIORITY RESEARCH DIRECTIONS

PRD 1: Enable Design of Revolutionary Molten Salt Coolants and Liquid Fuels

Key question: *How can we characterize and predict the structure, dynamics, and energetics of molten salts, including an evolving chemical composition across length and time scales?*

Over the past decade, efficiency, cost, and safety have motivated increased interest in the use of molten salts as coolants and fuels in next-generation nuclear reactors used for electricity generation and to supply high-temperature, low-pressure heat. The selection of the salt composition depends on the specific applications, fuel, and coolant and has numerous criteria and constraints. Consider solid-fuel salt-cooled reactors, wherein the molten salt flows over the solid fuel and removes heat to the primary heat exchanger and/or serves as the secondary coolant. In this case, the molten salt must have good thermal stability, good heat transfer and hydrodynamic properties, low vapor pressure and chemical reactivity, and chemical compatibility with the reactor materials. For a liquid salt–fueled reactor—in which fissile, fertile, and fission products are dissolved in the molten salt—the molten salt must further have good neutronics (i.e., a low neutron capture cross-section), radiochemical stability, and solubility of the fuel and fission products. To optimize the numerous (and in some cases conflicting) requirements of the physical, chemical, and radiochemical properties of molten salts for desired applications, new methods and tools are needed to characterize and predict their structure, dynamics, and energetics across length and time scales. These will lead to the development of new molten salt compositions with superior properties, which will directly impact the efficiency, safety, and operational lifetimes of next-generation nuclear reactors.

Scientific Challenges

The extreme operational conditions of molten salt coolants and liquid fuels challenge even state-of-the art experimental measurement and theoretical prediction. This difficulty limits understanding of the fundamental chemical and nuclear reactions and physical properties within these systems, and compromises the ability to optimize and leverage the full potential of advanced reactor systems. At any instant, the fluid may be heterogeneous and exist in localized equilibria that evolve in time as a result of dynamic chemical and nuclear processes. Complex speciation imparted by fission products and trace impurities has an unknown effect upon important properties, including heat and mass transfer, which in turn perturb the net thermodynamics, kinetics, and transport in both a chemical and physical context. One must account for the temporal evolution due to reactor events that include radiation absorption and scattering, nuclear processes (in which the fission and activation product chemistry is not completely known), and the presence of corrosion products that develop over time as a result of reactions of the liquid with the surrounding materials. Multiple time scales are relevant, from exceedingly fast nuclear events to the long-term behavior over the lifetime of the reactor. Concomitantly, many spatial scales must be considered—from the atomic-scale organization of molten salts about ions, to the mesoscale nucleation and growth of insoluble materials, to the macroscopic-scale impact on physical properties of materials and components within the reactor. Understanding of the relevant chemistry, physics, and materials science that must be transferred across coupled spatial and temporal scales is a critical factor. It underpins the needs for technological and scientific innovation that must be broadly reliable not only for science-based decisions but also for regulatory approval. The following are the essential scientific challenges:

- Understand the structure, dynamics, and thermodynamics of molten salts across the extreme operational conditions of advanced reactors.
- Understand and reliably predict the equilibrium phase diagrams and thermodynamic properties of multicomponent systems containing fission products and trace constituents.

- Characterize and describe the evolution of nonequilibrium systems.
- Develop high-throughput experimental methods to create thermodynamic data and incorporate these in interactive databases to guide molten salt selection.
- Understand the speciation and oxidation states of fission products and develop methods of monitoring the fission-driven changes to the local chemical potential to aid the development of predictive capabilities for long-term reactor behavior, including the role of transients.
- Elucidate the impact of fission and activation product chemistry upon salt properties, corrosion, and neutronics. This effort includes understanding corrosion and materials compatibility issues to predict and avoid system failures.
- Develop in situ and operando methods to characterize salt quality, impurities, and fission and corrosion products in real time to optimize reactor chemistry and operations.

Research Thrusts

To address the scientific challenges, this PRD identifies the following research areas that need to be pursued to provide the fundamental understanding necessary for the predictive design of new coolants and liquid fuels for future nuclear energy.

The structure and dynamics of molten salts in extreme environments and the connection between local behavior and macroscale properties

It is beginning to be possible to use average atomic-scale structure to understand and predict macroscopic properties for simple salts; however these approaches need further development to address multicomponent systems and added complexity involving minor and trace constituents, such as fission products and impurities. To understand the atomic-scale structure and dynamics of molten salts and their impact on chemical and physical properties—including viscosity, thermal conductivity, solubility, and vapor pressure—modeling and simulation must be coupled with advanced spectroscopic and scattering methods. Optical, Raman, and x-ray adsorption spectroscopy; nuclear magnetic resonance (NMR); and neutron scattering techniques are among those that can provide insights into the structure, coordination environment, and oxidation state of species in solution. For example, Figure 1 illustrates ab initio molecular dynamics (AIMD) simulations of a $ZnCl_2$ melt at 327°C alongside neutron diffraction and Raman measurements, which collectively indicate three major species present in the melt. [Alsayoud 2016]

An additional challenge is the in situ and operando measurement of molten salt properties under extreme environments (1000°C and higher in the presence of radioactivity). Recently, a high-temperature (up to 1000°C) airtight cell that can handle radioactive samples was developed for x-ray adsorption measurements of solid and molten actinide fluorides (Figure 2). This cell was used in high-temperature extended x-ray absorption fine structure measurements of LiF-ZrF_4 mixtures, which revealed the quantitative distribution of different anionic zirconium complexes. [Bessada 2017] Sample cells have also been designed for in situ spectroscopy and spectroelectrochemistry of actinides in high-temperature molten salts. [Polovov 2008] In addition, methods are needed for real-time monitoring of chemical and physical processes.

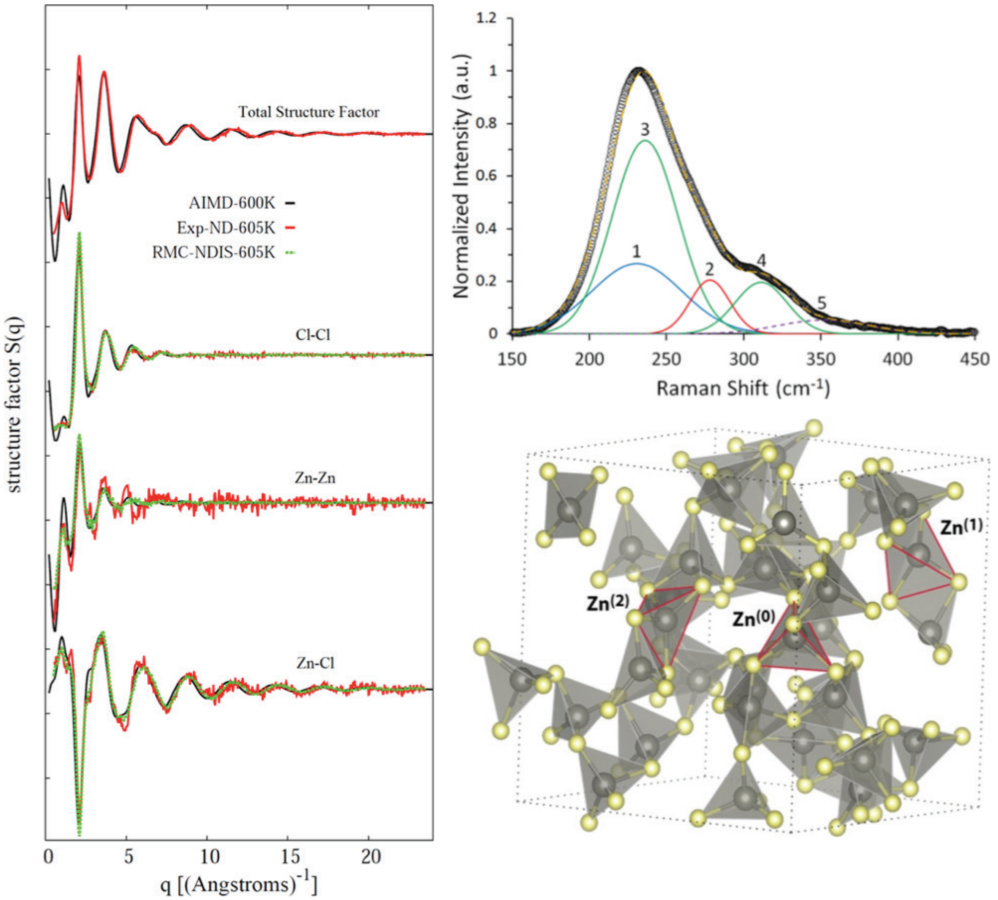


Figure 1. Coupled ab initio molecular dynamics with neutron diffraction and Raman vibrational spectroscopy to identify distinct polymorphs in $ZnCl_2$ molten solutions. | Reprinted with permission from A. Alsayoud et al. 2016. Structure of $ZnCl_2$ melt. Part I: Raman spectroscopy analysis driven by ab initio methods, *J. Phys. Chem. B* 120, 4174–4181. Copyright 2016 American Chemical Society

High-throughput measurements of phase diagrams and thermodynamic parameters of complex molten salt systems

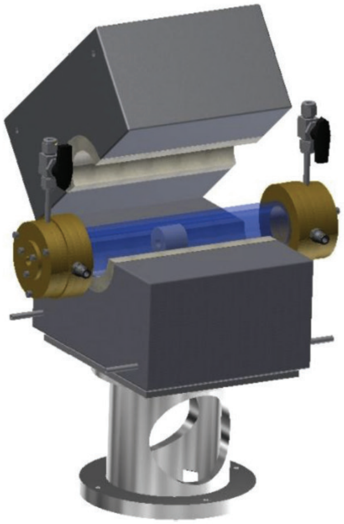


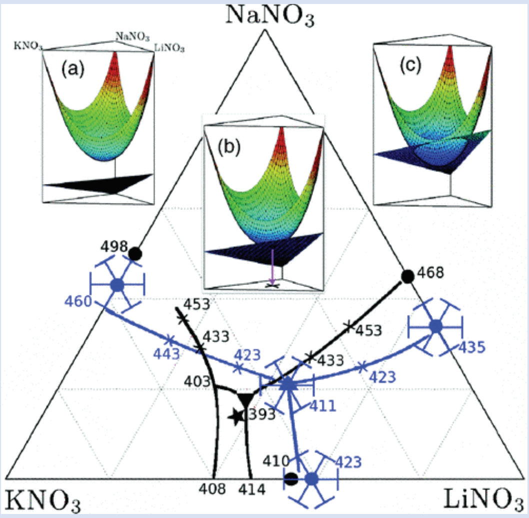
Figure 2. High-temperature cell for x-ray adsorption measurements of molten salts. | Reprinted from *J. Nucl. Mater*. 494, October, C. Bessada et al., High temperature EXAFS experiments in molten actinide fluorides: The challenge of a triple containment cell for radioactive and aggressive liquids, 192, copyright 2017, with permission from Elsevier

The phase diagram is the primary tool for understanding the phase behavior of molten salts, as it defines the temperature-composition space for a single-phase liquid (see the sidebar “Phase Diagrams”). Thermodynamic properties can be extracted from the phase diagrams (and conversely, phase diagrams can be constructed from thermodynamic data). Although phase diagrams can be determined by a variety of experimental methods, they tend to require a large

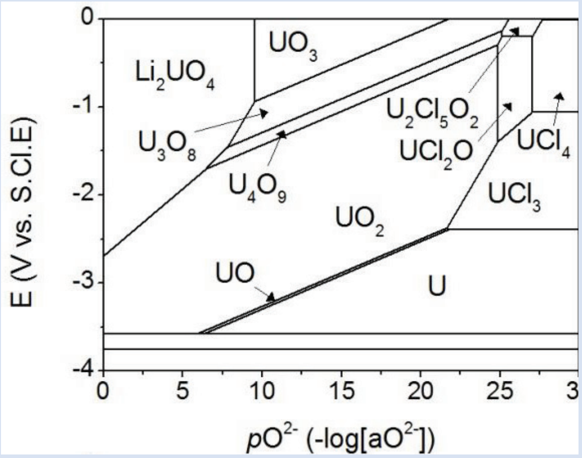
Phase Diagrams

Phase and predominance diagrams are graphical representations of free energy minimization, constrained by heat capacities, enthalpies, and entropies of formation/reaction. They provide details on speciation, phase transitions including melting, and dissolution and mixing of major and trace components in both the molten and solid phases. Such data can be obtained by experiment and by calculation from first principles or using more empirical potentials. An example of phase diagrams for the Li/Na/K nitrate ternary mixture is shown in the diagram below at left, with the calculated (blue) and experimental (black) eutectics. The blue lines represent binary eutectics in the presence of the third component and are not meant to depict the ternary phase diagram. The experimental and predicted phase diagrams are different; improvements are needed in the ability to accurately predict thermodynamics properties of molten salts.

Obtaining accurate thermodynamic data experimentally is labor-intensive and is done only by a small number of research groups. For complicated multicomponent molten salt coolants, the available data are grossly insufficient; for molten salt fuels, the situation is further complicated by the combination of high temperatures; radiation effects; and compositional change over time resulting from fission, transmutation, and dissolution of corrosion products. As a molten salt reactor operates, trace constituents that collect in the fluid phase can influence the chemistry of the salt matrix and the speciation of ions dissolved into the medium. One trace constituent is oxygen, which can significantly shift the speciation of both major and minor constituents. The generalized predominance diagram below at right shows the impact of oxygen on the redox chemistry for uranium in LiCl-KCl eutectic at 500°C. Note the complexity of the diagram.



Experimental eutectics in black and computed eutectics in blue. The black triangle, black curves, and black pentagram are ternary data, and the filled black circles are the binary eutectics. Crosses indicate temperature contours (K). Insets show the free energy of mixing for the liquid phase and the pure solid–liquid free energy difference connecting plane at three temperatures: T(a)<T(b)<T(c). | Reprinted from S. Jayaraman et al., Molten salt eutectics from atomistic simulations, *Phys. Rev. E*, **2011**, 84, 030201. Image courtesy of American Physical Society under the terms and conditions of the Creative Commons license.



Predominance diagrams of U, in NaCl-KCl at 750°C. | Reprinted from R. Abdulaziz et al. 2016. Predominance diagrams of spent nuclear fuel materials in LiCl-KCl and NaCl-KCl molten salt eutectics, | *Int. J. Electrochem. Sci.* 11, 10417-10435. Image courtesy of *Int. J. Electrochem. Sci*. under the terms and conditions of the Creative Commons license

number of high-purity samples; and there needs to be rigorous control (and measurement) of impurities, including dissolved metals, water, and oxygen-containing impurities (e.g., oxides, hydroxides, sulfates, carbonates, and oxyhalides). For liquid salt–fueled reactors, the impact of fission products (which include more than 40 elements) on the phase diagram must be determined. To address this challenge, we can build upon advances from the materials, high-temperature chemistry, and pharmaceutical industries to develop high-throughput approaches for screening candidate molten salts—with respect to properties like electrochemical potential, solubility, or heat transfer—and accelerate the development of new salt compositions. Knowledge of the phase transition, formation, and fusion enthalpies and entropies of the components and of the thermodynamic mixing properties of the melts is essential for accurate constraint of phase equilibria. In particular, thermodynamic parameters that enter databases and computational models must be grounded in experimental reality. Indeed, robust databases of a variety of thermodynamic properties could be revolutionary in this context. They should include

- Heat capacities from near absolute zero to operational temperatures
- Heats of mixing in appropriate molten salt systems
- Heats of fusion of common systems, including binary and ternary fluorides and chlorides
- Heats of dissolution of fission products and other impurities in molten salts, measured as a function of both molten salt composition and solute concentration

High-throughput methods that use calorimetry combined with spectroscopy or electrochemical methods need to be developed to handle radionuclides in air- and water-free environments. Experiments at moderate pressure may provide advantages in terms of suppressing volatility and overcoming containment problems, for example, by the use of a noble gas pressure medium in a diamond anvil cell. Levitation experiments, circumventing containment problems, may also be useful in determining phase diagrams and fusion enthalpies and in studying structure via neutron and synchrotron x-ray techniques. These and other new methodologies need considerable development, especially for application to extreme and corrosive environments that combine high temperatures and radiation fields.

Speciation and oxidation states of minor and trace constituents and their impact on molten salt properties

One of the challenges of a liquid salt–fueled reactor is that the chemical constituents are constantly changing because of the generation and decay of fission, activation, and corrosion products and the presence of impurities (such as dissolved metals, water, and oxygen-containing impurities). It is essential to understand which constituents are volatile, soluble, insoluble, or sometimes soluble in the molten salt and how they impact the properties of the salt. The thermophysical properties that directly impact heat transfer are strongly connected to the composition and impurity concentrations of the molten salt. Thus, optical spectroscopy, NMR, electrochemical methods, and x-ray and neutron scattering and spectroscopy are needed to understand the speciation and solvation of minor constituents in the molten salt and to understand their impact on properties and reactivity. For example, it was discovered in the Molten Salt Reactor Experiment (MSRE) that the fission product tellurium promoted cracking in the Hastelloy N reactor vessel by leaching chromium from the alloy. [Keiser 1977] Cracking may be reduced by controlling the redox potential of the salt through variation of the U^{3+}/U^{4+} ratio. Thus, methods are needed to provide real-time data on the changing composition (and properties) of the molten salt operando to optimize reactor performance. Since many of the nuclei are NMR-active, NMR methods could possibly be developed to monitor lanthanide ingrowth, as well as flow fields, viscosity, and diffusion coefficients. Given that many fission products are radioactive, initial studies could also focus on nonradioactive surrogates, i.e., stable isotopes of the elements.

One of the advantages of molten salt reactors (MSRs), and a reason for the increased interest in them, is their ability to burn actinides (for the production of electricity), which reduces the need for geologic storage of spent nuclear fuel. This opportunity also creates additional technical challenges in understanding the solution-phase chemistry and reactivity of actinides. For example, the Molten Salt

Advanced Reactor Transmuter (MOSART) reactor, one of the designs actively being considered that would encompass complete actinide transmutation, uses transuranic trifluorides (Np, Pu, Am, and Cm) from light water reactor spent nuclear fuels as the fuel in a mixture of LiF (15 mol %), NaF (58 mol %), and BeF_2 (27 mol %). The fraction of actinides transmuted in 60 years is 91–92%, but heavier actinides (including Cf and Bk) are also produced during the lifetime of the reactor. [Forsberg 2003] The actinide component can be divided into two regimes—the light actinides actinium through plutonium, and the heavy actinides americium through fermium.

The light actinides have electronic properties that parallel those of the transition metals owing to the radial extension of the 5f electrons beyond the valence shell. As the actinide series is traversed, relativistic effects alter the spatial availability and energetics of 5f, 6d, and 7s orbitals, which drive actinide reactivity under conditions relevant to MSRs. The challenges for the lighter actinides center on the directed management of oxidation states to enable in situ separations. To minimize corrosion and enable online actinide recovery via pyroprocessing, these actinides are trivalent while in the molten salt solution. Although the trivalent state is common for the heavier actinides, uranium through plutonium generally persist in higher oxidation states, and knowledge of the behavior of their trivalent state is limited. This lack of understanding impedes the ability to predict actinide speciation and redox chemistry in molten salt systems. As an example, the chemistry of trivalent protactinium is highly relevant to the thorium fuel cycle (in which ^{232}Th is transmuted into ^{233}Th, which beta decays to ^{233}Pa and then to the fissile ^{233}U), yet facilities and isotopes available for work with protactinium are both limited. Only recently has the speciation of protactinium fluorides been probed, wherein the PaF_8^- anion is proposed to be the predominant Pa(V) complex in concentrated solutions of aqueous hydrogen fluoride (Figure 3). The challenges for the heavier actinides stem from limited knowledge of their chemistry, especially in the extreme conditions of MSRs. The chemistry of transcurium actinides, including tetravalent berkelium, and of divalent elements heavier than berkelium, is relevant to predicting the chemistry controlling both equilibrium and nonequilibrium phenomena in these systems.

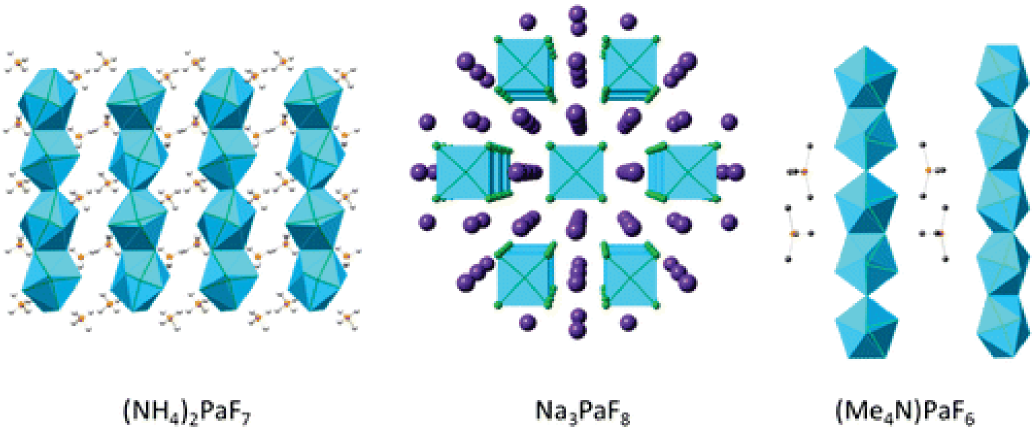


Figure 3. Select protactinium(V) fluoride structures synthesized in De Sio and Wilson 2014. | Reprinted with permission from S. M. De Sio and R. E. Wilson. 2014. Structural and spectroscopic studies of fluoroprotactinates, *Inorg. Chem.* 53(3), 1750–1755. Copyright 2014 American Chemical Society.

Data-driven advances in computational models and methods for predictive understanding of the structure, dynamics, and thermodynamics of molten salts

The development of predictive methods and algorithms for studying salt chemistry is a major scientific challenge. This is the case because of (1) the complex nature of the salt mixtures and (2) the dynamic salt composition due to the production and decay of fission products, and its impact on chemical reactivity and physical properties across length and time scales. Quantum mechanics and classical dynamics—combined with coarse-grained, continuum, and thermodynamic models and validated with experimental data—will achieve predictive insights into solvation, speciation, and chemical reactivity from the atomic scale to bulk thermophysical and transport properties at longer length and time scales.

Few studies are reported on molten salts that are based on first principles electronic structure calculations and are capable of explicitly treating polarization effects and chemical reactivity. [Bengston 2014; Song 2017] Classical interatomic potentials have been applied with some success to predict molten salt properties. [Jabes 2012; Dewan 2013; Luo 2016; Nam 2014; Song 2017] Here, the MSR salt fuel can be treated as a set of cations that are changing their identity (through nuclear transmutation and fission) and their oxidation states embedded in a sea of fluoride or chloride anions. The current approach is to fit a classical potential model to a set of results from first principles electronic structure calculations, with improved parameterization from available liquid state data. This suffices only if configurations can be sampled and there are no changes in the oxidation state or the valency; however, for more complex systems, many different force field interactions will be needed, with a concomitant increase in complexity. Thus, fundamentally different approaches are required to address the issue of dynamic time- and space-dependent chemistry.

For application to heavy elements, all electronic structure methods must include relativistic effects; yet the accuracy of these approaches is not uniformly robust. Actinides in lower oxidation states have many close-lying electronic states in which the electrons mix within the 7f orbitals, resulting in a rich multiplet structure with implications for the electronic properties of molecules. The modeling of redox reactions (critical for speciation) requires the ability to treat different numbers of f electrons at the same level of accuracy, but currently this cannot be done. These fundamental limitations—which are ultimately all related to the inability of current electronic structure methods to capture the multiple ways f electrons can interact with one another, with electrons in other shells, and with their surrounding environment—need to be addressed to advance understanding of the structure, solvation of ions, and thermodynamics of molten salts.

Molecular dynamics (MD) simulations are needed to predict the structure and dynamics of salts in the bulk and at the salt/reactor and salt/vapor interfaces. They can be used to predict and explain transport properties, as well as explain the origins of features found in x-ray and neutron structure factors and radical distribution functions. First principles MD simulations of pure molten salts at multiple temperatures are needed to obtain temperature-dependent thermodynamics, kinetics, and transport properties; and speciation is needed for the prediction of phase diagrams and other physical properties. Innovative approaches to long-time MD sampling are needed to predict nucleation, [Kathmann 2009; Kathmann 2006] releases of volatiles, and rates of reactions, including redox reactions. Knowledge of the constituents is needed to understand interfacial behavior leading to MSR material degradation, i.e., corrosion. At longer length and time scales, integration of thermochemical information into higher-order (multi-element) systems is critical to predict complex liquid and solid solution behavior. Thermophysical and transport properties, such as thermal conductivity and viscosity, are needed for the modeling of material flow that is required to model fissile reactions and MSR performance. Such computational studies will require large simulation sizes, on the orders of tens of millions of atoms, to cover the required spatial scale. This will require access to DOE's highest-performance computers and optimized exascale software.

With the development of new methods for high-throughput data collection and the availability of databases, new computational methods and approaches are needed to query and visualize phase diagrams and thermodynamic data. Thermodynamic models are needed to predict properties beyond conditions that can be experimentally measured, such as in highly radioactive samples. These advances would accelerate the development of new molten salt systems and provide the data needed for the design of an MSR.

Uncertainty quantification is a unifying feature for all the development described above. It is critical to provide error bars from the computations (as well as from experiments), either through careful analysis of each term in the modeling or through proper sampling. New applied mathematical approaches are needed for computationally more efficient uncertainty analysis.

Potential Scientific Impact

MSRs use molten salts as the primary coolant at atmospheric pressure. Either the molten salts can flow past the solid fuel to remove heat to the primary heat exchanger, or the fuel can be dissolved in the molten salt that flows through the primary heat exchanger. For molten salts to be used in future nuclear energy applications, significant fundamental scientific challenges must be addressed to advance the understanding of the structure, properties, and reactivity of molten salts and the solvation of actinides and fission products. Addressing the proposed research directions will enable the following scientific impacts:

- The design and synthesis of new salt-based coolants and fuels based on fundamental knowledge of the physical and chemical properties of the individual components
- Predictive understanding of the impacts of minor and trace solutes on physical and chemical properties of molten salt fuels
- Development of high-throughput characterization methods that may be applicable to other fields of study
- Improved understanding of actinide chemistry and identification of new emergent behavior for heavy elements in extreme environments
- Advances in experimental methods to measure properties in situ and operando under extreme environments
- Advances in computational methods to address f element chemistry, and validated predictive models of structure, dynamics, and properties that bridge length and time scales, which are applicable to many problems across DOE’s research portfolio

Potential Impacts on Energy Technology

There is significant worldwide interest in the development of MSRs because they provide new opportunities to rationalize the nuclear fuel cycle by using a variety of fissile (^{233}U, ^{235}U, or ^{239}Pu) and fertile (^{232}Th or ^{238}U) materials to supply cost-competitive, safe, nuclear electricity generation and high-temperature, low-pressure industrial heat. However, a fundamental lack of understanding of how the changing chemical composition of a molten salt changes the salt’s chemical and physical properties—and the subsequent impact on the reactor design parameters, operational parameters, and lifetime—is one of the many factors that has hindered the development of liquid salt–fueled reactors. Addressing the scientific challenges discussed in this PRD will provide the scientific foundations necessary to allow the development of compact high-temperature reactors enabling safe, cost-effective electricity generation and excess heat for other uses such as desalination and hydrogen production. New molten salts will be developed for fluid-fueled reactors compatible with a variety or fissile or fertile fuels, allowing a reduction in the amount of spent nuclear fuel. The fundamental knowledge and advances gained for in situ and operando characterization will also provide new insights into reprocessing methods, corrosion, and optimal reactor operation.

Molten salts are also envisioned as coolants, in the primary or secondary loop, for high-temperature (600–1000°C and beyond) nuclear reactors that will be more efficient. This research will lead to improved high-temperature fluids with superior heat transfer properties for other applications, e.g., solar thermal energy.

PRD 2: Master the Hierarchy of Materials Design and Synthesis for Complex, Reactor Environments

***Key question:** How do we design, synthesize and process superior materials able to function and perform over decades in the extreme environments of advanced nuclear reactors?*

Future nuclear reactor systems will require a new generation of materials designed to withstand extreme environments, including materials designed with hierarchical architectures incorporating multidimensional phases with complex alloy or compound chemistries. Developing such materials calls for an approach to accelerate the discovery and design of materials for performance under coupled extremes, leveraging advanced experimental techniques and modern data science approaches. The synthesis of materials with targeted microstructures is also a critical component for scaling from atomistic to ensemble responses and developing predictable microstructural pathways and performance. This PRD will enable high-throughput science for the discovery and design of materials to meet the needs of future nuclear energy systems. A key challenge is to bridge from atomistic mechanisms to the collective responses of hierarchical architectures under coupled extremes.

Scientific Challenges

The scientific challenge is to elucidate the underpinning science enabling the design of radiation-resilient materials that possess emergent phenomena that exploit multiple length scales, including interfacial metastability, hybrid architectures, and/or complex chemistries. The predictive design of materials requires fundamental understanding of thermodynamic and kinetic pathways in chemically and structurally diverse material architectures that are far from equilibrium. The key elements of the scientific challenges embodied in this PRD include

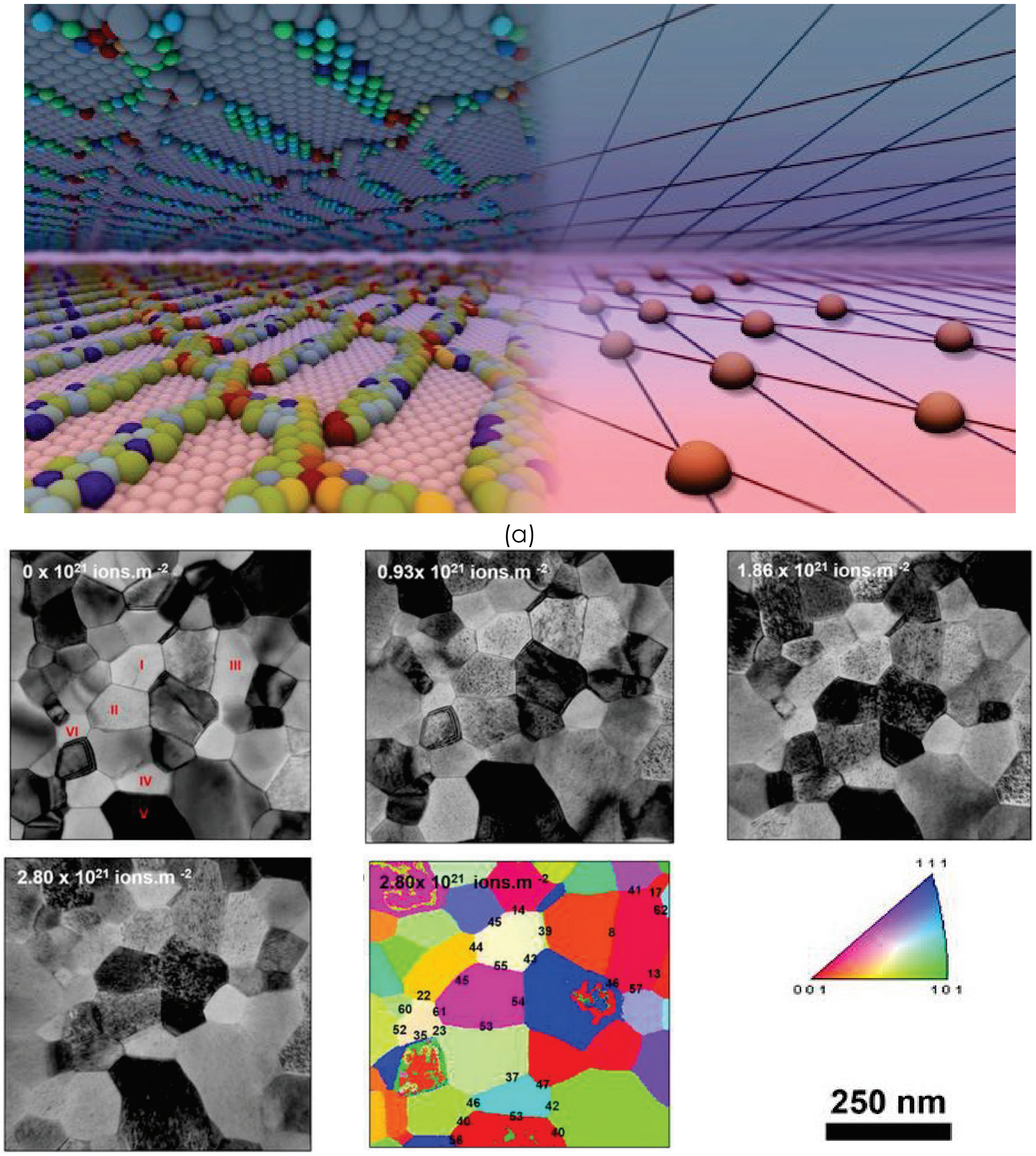
- Bridge from atomic-scale defect and interface mechanisms to collective response of microstructures under coupled extremes
- Predict kinetic and thermodynamic pathways to enable microstructural design for extreme environments
- Design new synthetic processes to produce tailored microstructures
- Develop accelerated testing approaches with tightly integrated feedback between modeling and experiments

Research Thrusts

To address the scientific challenges outlined, the following research thrusts are provided to inspire fundamental research required for the design of next-generation radiation-resilient materials required for future nuclear energy concepts.

Bridge from atomic-scale defect and interface mechanisms to collective response of microstructures under coupled extremes

In structural materials and fuels, internal interfaces, such as grain and interphase boundaries, are heterogeneities that serve as sites for a large number of synergistic phenomena that can either anneal and reduce, or nucleate and grow damage. Impeding our understanding of the complex interfacial changes taking place under extreme environments are the vastly different time and length scales over which these mechanisms operate and the resulting manifestations of damage occur. Therefore, it is highly desirable to design interfaces that are adaptive to these extreme environments and that serve to heal, as opposed to accumulate, damage. However, to reach this goal will require a fundamental understanding of atomistic mechanisms taking place at the single interface level, as illustrated in Figure 4a [Vattré 2014] and by recent progress in understanding fundamental unit mechanisms of defect-interface interactions in irradiated materials. [Beyerlein 2013]



(a)

(b)

Figure 4. (a) Computational design of patterned interfaces using reduced order models. | Image courtesy of Massachusetts Institute of Technology. Reprinted from Vattré et al. 2014. Computational design of patterned interfaces using reduced order models, *Sci. Rep.* 4, 6231 under the terms and conditions of the Creative Commons Attribution 4 license. 2014 (b) Analysis of defect accumulation at the microstructure level to establish correlations between damage state, grain orientation, and grain boundary properties. | Reprinted from El-Atwani et al. 2017. Direct observation of sink-dependent defect evolution in nanocrystalline iron under irradiation, *Sci. Rep.* 7, 12 under the terms and conditions of the Creative Commons license

Bridging to the complexity introduced by the different elements that compose a microstructure ensemble—as captured in Figure 4b, which shows the defect accumulation relevant to the grain boundary network [El-

Atwani 2017]—represents a synergistic understanding needed to design tailored microstructures for predictable properties. Therefore, the following are the scientific questions that must be addressed:

- How do we understand the full range of defect and interface mechanisms induced by coupled irradiation extremes across broad length and time scales?
- How do we harness emergent phenomena at mesoscales in far-from-equilibrium microstructures to reduce or repair damage?

To address these questions, advances are required in the ability to design and synthesize specifically tailored microstructures, which will enable the examination of the ensemble response of these novel hierarchical materials. New computational tools also are necessary to bridge atomistic phenomena at adaptive interfaces to phase-field or other mesoscale models of microstructure evolution. Finally, new frontiers in 3D and in situ quantitative characterization techniques in coupled environments are critical to understanding mechanisms across nano- to meso-dimensional and temporal scales.

Predict kinetic and thermodynamic pathways to enable microstructural design for extreme environments

A fundamental understanding of the thermodynamic and kinetic pathways that determine microstructure evolution is needed to develop design principles for material design for extreme environments. The key scientific questions include

- How does microstructure influence transport and physical properties?
- How does microstructure influence radiation resistance?
- How do properties evolve in a dynamically complex microstructure under highly transient conditions?
- How does the structure-property relationship change under coupled extremes with far-from-equilibrium conditions?

A critical need thus exists to establish microstructure-property relations that will enable materials design and result in predicable performance that targets specific properties and/or attributes (e.g., thermal conductivity, radiation stability, and fission product retention). The ability to fabricate designed microstructures represents an essential first step required to fully evaluate these attributes in the context of kinetic and thermodynamic pathways. Further, capturing and interpreting the full range of data from these experiments will require the integration of data science approaches and machine learning techniques to accelerate the fundamental understanding of designer microstructures and their implications for long-term performance during reactor lifetimes.

Design new synthetic processes to produce tailored microstructures

The realization of next-generation structural materials and nuclear fuels will require novel synthetic methods. Critical to this goal is the understanding of the fundamental mechanisms of phase metastability that are governed by kinetic pathways—rather than thermodynamically favored pathways—specifically to enable the formulation and synthesis of new phases. Building on current efforts using kinetically driven microstructure modifications—such as irradiation, [Bellon 2015] additive manufacturing, [Gu 2012] and extreme deformation [Arshad 2015]—novel microstructures can be fabricated to answer specific fundamental questions regarding material resistance to degradation under coupled extremes. Similarly, using gamma irradiation in aqueous solutions has enabled chemistry to be driven by solvated electrons formed in solution, as depicted in Figure 5; the strength of the irradiation dose correlates with the concentration of solvated electrons formed, thereby dictating the reduction routes of the synthesis. [Belloni 2006] Uniform non-thermodynamically predicted AgNi alloy nanoparticles of predesigned stoichiometries have been successfully synthesized and characterized, [Zhang 2010] and this method has been extended to nuclear fuel compositions. [Nenoff 2013]

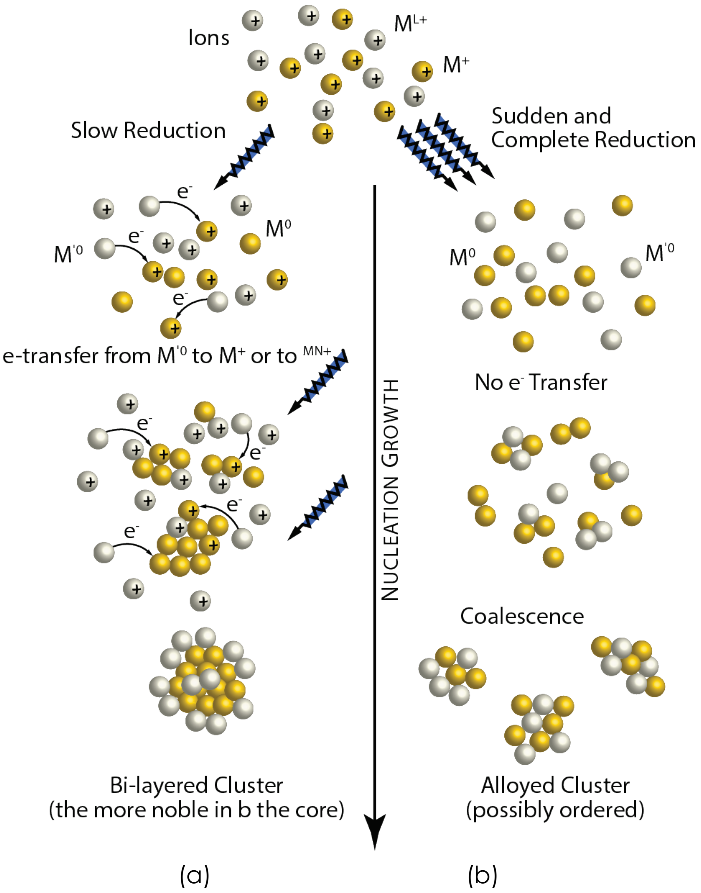


Figure 5. Radiation pathway for nanoparticle and alloy synthesis. | Reprinted from *Catal. Today* 113(3–4), J. Belloni, Nucleation, growth, and properties of nanoclusters studied by radiation chemistry: Application to catalysis, 141–156, copyright 2006, with permission from Elsevier

To develop advanced synthesis methods, however, will require an understanding of reaction mechanisms for a number of future materials needs, including targeted self-healing properties based on defect sink strength and defect reaction kinetics. Examples of successful materials development would include the ability to immobilize fission gases into the fuel (thereby minimizing environmental contamination) or design defect sinks into structural materials. This need lends itself directly to the use of high-performance computing to model and predict events such as metal/gas interactions, defect growth, and nanoscale structures. Not only will fundamental research be enabled by this predictive capability, but also the simultaneous development of computational toolboxes will enable the continuous and ever-more-complex design of novel advanced materials combining material neutronics, thermodynamics, kinetics, reversible chemistry, and quantitative microstructure description. It is thought that the exploitation of combinatorial chemistry and big data can propel the exploration of novel materials' compositions for intrinsically safe fuels.

Develop accelerated testing approaches with tightly integrated feedback between modeling and experiments

Under the steady state operation of a reactor, core materials may exhibit dramatic changes in behavior. The transitions are characterized by a sharp departure in the rate of evolution of the microstructure. As this change is dependent on many operational and material variables, understanding the mechanisms controlling these events and predicting them remain major challenges. For example, void swelling undergoes an extended incubation period that is interrupted by a rapid acceleration of the swelling rate. Such observations have been made in both metallic alloys [Zinkle 2013] and fuels [Iltis 2017] as demonstrated in Figure 6. As the timing of this rate change is dependent on many operational and material variables, it is very challenging to predict it. Other examples include precipitate formation in reactor pressure vessel steels [Ke 2017] and breakaway irradiation growth/oxidation in Zircaloys. [Garner 2007]

Conversely, changes in external stimuli can induce changes in the rate of microstructure evolution or property behavior (hot spots). These may be rare or frequent events in which the temperature, neutron flux, and coolant chemistry undergo a transient or excursion that induces changes to the microstructure.

An example is a temperature excursion that induces the nucleation of defects or anneals out existing defects, thus altering the subsequent evolution of the microstructure. This effect was evident during shutdown of a fast-flux test facility, where a slow temperature change resulted in the nucleation of a fine array of dislocation loops that significantly changed both the sink strength and sink nature and hardened the alloy. [Garner 1993] Other examples are changes in coolant chemistry, such as an excursion in the dissolved oxygen content, or an increase in water conductivity due to the unintentional injection of ionic species into the coolant. Such changes induce an alteration of the growing oxide and can dramatically alter processes such as localized corrosion or stress corrosion crack growth.

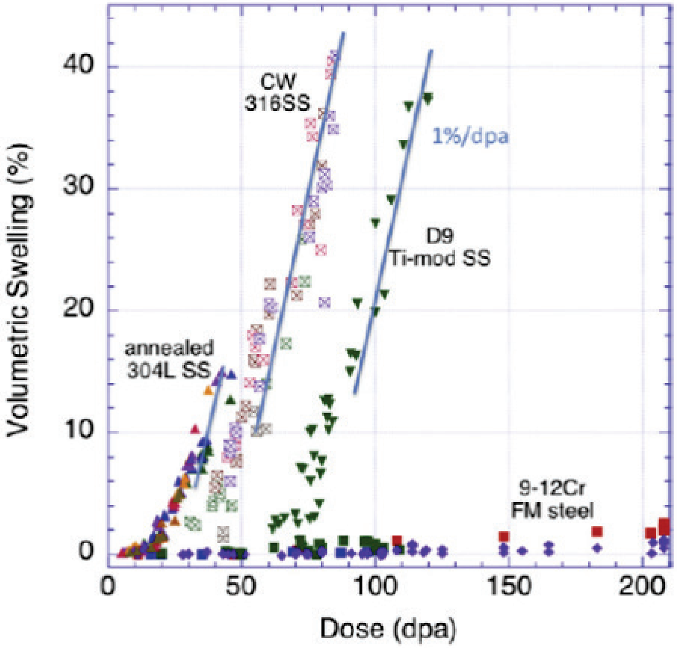


Figure 6. Cavity swelling in iron base cladding alloys. | Reprinted from *Acta Mater*, 61(3), S. J. Zinkle and G. S. Was, Materials challenges in nuclear energy, 735–758, copyright 2013, with permission from Elsevier.

Regardless of the driver, these events will dictate the course of microstructure and property evolution after their occurrence, so that microstructure evolution will follow a different path from what it would have taken in the absence of the event. Thus, there is a great need to develop the capabilities to predict the occurrence of these microstructure discontinuities and the ensuing evolution of the microstructure.

A fundamental challenge is to understand these threshold/hot-spot/slope-discontinuity processes, whether they are intrinsic to the process or stimulated by an external event. The question then is how to design experiments and simulations to discover these physical processes. Specifically, can accelerated testing (computational/experimental) techniques be developed to predict rate changes in the microstructure of a material under steady external conditions (temperature, stress, chemistry, flux)? Further, can experimental/simulation techniques be developed to assess how the rate of microstructure evolution changes with external stimuli (temperature, stress, chemistry, flux)? In both cases, new experimental techniques are needed to allow validation of the developed computer simulations. Researchers must also be able to identify regimes in which rates of microstructure evolution change dramatically with microstructure or stimuli. A major challenge is to develop these techniques and the underpinning models to span large time scales and determine microstructure evolutions efficiently over entire lifetimes. Such advancements (validated tools as well as locations of thresholds and hot spots) will enable improved alloy design (e.g., composition, microstructure, processing).

Potential Impacts

Mastering hierarchical architectures has the potential to greatly impact the design, development, operation, and safety of advanced nuclear energy systems. The impact will manifest itself in two forms:

1. Advanced multiscale models to assist with the design and development models
2. New fuel, structural, and functional materials that permit reactors to operate at higher flux and temperature, allowing longer lifetimes and smaller evacuation zones around advanced nuclear reactor systems

Every advancement in experimentally validated models and development of new materials containing hierarchical architectures provides an additional tool to increase the confidence in the regulatory process of any advanced nuclear reactor systems put into operation.

PRD 3: Tailor Interfaces to Control the Impact of Nuclear Environments

Key question: *How can the multitude of inextricably linked chemical and physical processes that occur at interfaces be controlled?*

The requirements for nuclear power plants with long lifetimes and high reliability demand understanding of the chemistry and materials science of dynamic interfaces under extreme conditions far beyond our current knowledge. These interfaces, including solid/fluid and solid/solid ones, play critical roles in enhancing the performance of coolants (gas and liquid) and solid materials in reactor systems. Interfaces provide pathways for efficient heat transfer, are preferential sites for chemical reactions, and oftentimes are places where materials failure is initiated. The confluence of the development of modern computer algorithms, new computer architectures, and advanced nanoscale characterization tools provides exciting opportunities to discover the fundamental science of how complex interfaces evolve under radiation, high-temperature, high-stress, and corrosive environments, and to lay the foundation for the design of next-generation materials and coolants to support future nuclear energy technologies.

Understanding, controlling, and even tailoring interfacial processes—whether at the fluid coolant/solid interface or the solid/solid interface resulting from propagation of corrosion fronts—is critical to future nuclear energy technologies because these processes ultimately determine material reliability. Clarifying the collective effects of radiation-induced reactions at interfaces and of thermal interactions under the anticipated conditions of new reactor technologies requires knowledge well beyond our current understanding established on water-based reactors. Mastering these processes is particularly urgent because future nuclear reactor concepts involve the development of new materials and extreme operating conditions about which little of the fundamental science is currently known. An added complication beyond the extreme conditions is the presence of corrosion products at the interface and of suspended nanoparticles (generated by radiolysis and corrosion processes), which can enhance radiolytic damage rates and yields in a manner that is not currently predictable.

Radiation effects represent an important part of this PRD. Radiation damage in materials, at both surfaces and interfaces, arises both from energy losses associated with electronic excitations and ionizations, and from nuclear displacements. Electronic excitations and ionizations mainly result from the inelastic scattering of low-energy electrons produced by higher-energy particles, such as gamma rays, x-rays, (recoil) protons, and alpha particles. Nuclear displacements arise from momentum transfer and recoil events in ballistic nuclear collisions. Radiation effects induce chemical changes in the coolant and driving processes at the coolant/solid interface, leading to corrosion that extends from nanometers to millimeters into the material. Although coolant chemistry and bulk corrosion have typically been considered separately in the past, they are intimately connected; future research must address them as a system. For example, there is a systematic mechanistic path connecting radiation-driven chemistry at the coolant/solid interface to the moving oxidation fronts typical of corrosion. The same processes that cause radiation-induced loss of atoms from the solid surface into the coolant often correlate with enhanced motion of point defects in protective layers and penetration of corrosion into the material. As shown in Figure 7, the effect of radiation on corrosion can depend considerably on the coolant composition and the presence or absence of air. Radiation also introduces a flux of point defects to solid/solid internal interfaces, e.g., grain boundaries and precipitate/matrix interfaces, which cause structural and compositional modifications. Furthermore, the accumulation of radiation-produced damage within the interior of a grain modifies the deformation response. The consequences of these modifications can have a profound and negative impact on the structural integrity of the component. For example, dislocation interactions with grain boundaries are important in rupturing the oxide and exposing the bare metal to the coolant—a critical component in irradiation-assisted stress corrosion cracking. Current understanding of deformation processes in irradiated metals and the resultant decrease in mechanical properties is limited to the operational conditions of water-cooled reactors.

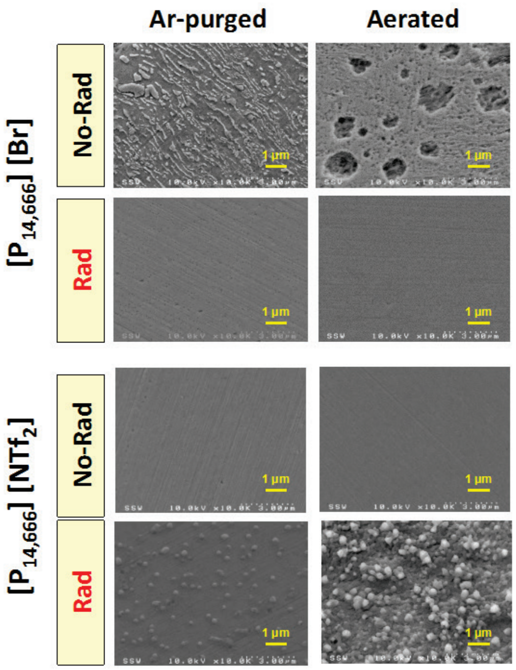


Figure 7. Example of coupling between radiation effects in coolant and corrosion of the base solid. Above, γ-irradiation suppresses the intrinsic corrosion of carbon steel by the ionic liquid $[P_{14,666}]$[Br]. Below, radiation in the presence of air accelerates corrosion of the same steel in normally unreactive $[P_{14,666}]$$[NTf_2]$. | Reprinted from *Corros. Sci.* 102, R. P. Morco et al., Corrosion of carbon steel in the $[P_{14666}]$ [Br] ionic liquid: The effects of gamma-radiation and cover gas, 1–15, copyright 2016, with permission from Elsevier

Scientific Challenges and Opportunities

Understanding energy, charge, and heat transport processes at solid/fluid (gas and liquid) interfaces in nuclear reactor environments

Absorption and dissipation of radiation energy arising from the exchange of energy, charge, and reactive species between the phases is significantly more complicated in heterogeneous multi-phase systems than in homogeneous systems. The basic mechanisms of these processes are poorly understood; yet they can lead to dramatic transformations of surface and subsurface layers of the material, as well as the contacting fluids. Special attention must be paid to the reactive intermediates at the interface, including surface defects, active groups, and specific adsorption complexes. These intermediates can be created directly and locally at the interface, or from the mobile electronic excitations or reactive species generated radiolytically in the subsurface layers of the material and trapped at the interface. These sites can be major focal points for interfacial charge transfer, initiating a broad range of processes at interfaces, such as corrosion.

Important processes that occur at the solid–fluid interface under the radiation conditions typical of reactors include

- Enhanced radiolysis, due to energy and polaron (hole/electron) transfer from the solid phase, of the fluid coolant at or near the surface of the structural materials (and nanoparticles dispersed in the fluid). It leads to enhanced evolution of products (e.g., O_2, H_2, Cl_2) that may alter the chemistry of the coolant.
- Dissolution of the solid material (metal, oxide, or ceramic) into the fluid, which contaminates the coolant and alters properties of the structural materials.
- Erosion and defect formation on the surface of the material leading to uniform or local degradation after long operation cycles.
- Material restructuring and/or elemental segregation that changes the surface reactivity with respect to the coolant.
- Damage to protective layers/coatings that may lead to complete loss of their protective properties.

Comprehending the mechanisms of these interrelated processes will require in situ and operando experimental techniques that are closely coupled to the insights provided by theory and multiscale computational methods.

Mastering corrosion processes under extreme thermal and radiolytic conditions

The ultimate vision for controlling corrosion would be to develop an understanding of the kinetics of corrosion for any microstructural unit and establish a set of design rules and synthesis processes for combining microstructures to produce a thin, impervious, protective, and stable protective film for any specific environment.

Important phenomena that need to be understood to reach this vision include

- Competition between thermodynamics and kinetics in driving the formation and movement of the corrosion front
- The effects of physical heterogeneities on the competition between local thermodynamic and kinetic drivers
- Changes to local electronic effects caused by dilute impurity atoms
- Differences caused by external factors, such as radiation, that create nonequilibrium structures, or coolants that change kinetics or thermodynamics at surfaces

Chemistry of solid–fluid interfaces in extreme environments

Understanding and controlling physical and chemical effects occurring at interfaces are extremely important for the development and deployment of the next generation of nuclear reactors. However, intense radiation fields, high temperatures, and above-atmospheric pressures lead to highly nonequilibrium environments that have not been fully considered. Much of our knowledge of the processes that occur at interfaces is empirical. A detailed fundamental mechanistic understanding of the myriad of processes that occur in these complex environments is necessary to obtaining a predictive understanding that can be applied to the design and development of new materials and coolants for advanced nuclear reactors. Emerging technologies in both the experimental and theoretical fields offer huge potential for achieving the goals of understanding and controlling the fundamental chemical and physical processes occurring at interfaces.

Radiolytic processes occurring at solid/fluid interfaces may be initiated either by direct energy deposition in the local region or following the transport of energy, mass, or charge through either phase to the interface. The efficiency of energy and charge transfer events at solid/fluid interfaces depends upon the chemical compositions of the fluid, as well as the interface terminations, microscopic structure, nanoparticle phases, and dimensions of the material. Processes initiated on a short time scale can also manifest themselves at much longer times and at distances far removed from the initial energy deposition site. This multiscale nature poses great challenges in obtaining realistic mechanistic information, as well as in predicting future events.

The elucidation of radiolytic processes at heterogeneous solid/fluid interfaces presents even more challenges. Energy and polarons induced in either phase by incident radiation can migrate to and across the interfaces, inducing damaging radical and redox chemistry in the coolant and corrosion in materials. The transport mechanisms of energy, mass, or charge through the interface are often unknown and difficult to quantify. For example, the energy transport mechanism through the interface depends upon the degree of electron-phonon coupling. Strong coupling leads to heating and thermal processes. Weak coupling enables localization of electronic energy, leading to nonthermal damage and desorption processes.

A wide variety of interfaces (solid/liquid, solid/gas, and liquid/gas) will exist in advanced nuclear energy systems. The anticipated high operational temperatures will require the design and discovery of new materials and coatings for both fuels and structural components. There are many classes of materials that may be considered, including ceramics, graphite and carbides, MAX phase materials (layered carbides and nutrides), and metallic glasses. With respect to coolants, helium is the most common gas proposed for solid/gas reactors because of its chemical inertness at high operating temperatures. Although helium itself is chemically inert, reactive impurities such as O_2, N_2, H_2O, CO, and CO_2 (as well as possibly a variety of small hydrocarbons) will be present in small quantities and will pose challenges in interfacial chemistry. In molten salt and liquid metal reactors, solid/liquid interfacial chemical processes will dominate; however, vapor phases—as either head space, an interfacial layer, or bubbles (produced by fission gas, cavitation, chemistry, or temperature excursions)—would be expected in high-temperature environments. The wide range of chemical and physical processes that occur at solid/fluid interfaces must be understood to meet the demands of advanced nuclear reactors.

Understanding how irradiation-induced defects impact solid/solid interface response to stress

Internal solid/solid interfaces such as grain and phase boundaries play a determining role in the response of materials to stress and radiation-induced changes in microstructure and composition. These interfaces act as sinks for point defects, solutes, and impurities; and the ability of the interfaces to effectively absorb these strongly influences the radiation resistance of the material. For example, the development of nanostructured ferritic alloys—which contain a very high density of nanostructured oxide features, small grains, and a high dislocation density—results in an increase in the resistance to radiation damage and an improvement in the creep properties. [Odette 2018] Similarly, introducing a large number of interfaces, as in a multilayered composite of dissimilar metals, has been shown to enhance the radiation resistance. [Misra et al. 2007] Interfaces also dictate the mechanical response, serving as both sources of and sinks for dislocations, as sites of stress concentrations that ultimately become failure initiation sites, and as failure pathways for some instances of environmental assisted cracking. The responses of these interfaces are dependent on compositional and structural modifications that are driven by point defect fluxes and dislocation interactions, by temperature, by stress, and by the local environment. For example, grain boundaries serve as the sources of dislocations that produce deformation channels in a deformed irradiated metal. The interaction of these channels with grain boundaries and the transfer of strain across them, at least at low levels of strains and below 350°C, is governed by the same rules as in unirradiated metal, except that the magnitude of the local stress must be sufficient for the dislocations emitted from the grain boundary to overcome the radiation-produced obstacle field and propagate away from it. [Cui et al. 2014]

There is a paucity of information on how these processes are modified at large strains and stresses, high damage levels, and high temperature, and on the continuous evolution of the composition and structure of the interfaces. Similarly, there is a need to understand how the evolution of precipitates under extreme conditions impacts the structural integrity of the metal. The fundamental processes by which these interfaces react to the external stimuli that will occur in advanced reactor designs must be revealed so that processing strategies can be developed to optimize not the initial but the evolved structure, composition, and properties of the interfaces to ensure long-term structural integrity. This will entail novel combinations of modeling, simulation, advanced microstructural characterization, and smart processing to determine how to control and manipulate interfaces to achieve the desired properties.

Advances in experimental techniques

Experimental techniques for probing interfacial phenomena, especially in situ and operando, are required to understand interfacial processes that occur in the extreme environments anticipated for advanced nuclear reactors. Recent advances in characterization tools—especially spectroscopic, imaging and scattering techniques—have made it possible to examine mechanisms responsible for radiation damage at interfaces across the spatial and temporal scales relevant to energy transfer, strain transfer, and chemical reactivity. For example, new experimental techniques that span ultrafast (attosecond) time resolution and ultrahigh spatial resolution (a few angstrom) are rapidly evolving. These include, but are not limited to, the following tools:

- Time-resolved ultraviolet, VIS, mid-infrared, and Raman spectroscopy
- High–spatial-resolution x-ray and neutron probes and 3D x-ray microscopy
- Time-resolved and ultrafast x-ray probes
- Time-resolved electron microscopy and 3D electron tomography
- Atomic force microscopy and other imaging techniques in situ under irradiation
- 3D compositional analysis via techniques such as atom probe tomography

As an example, novel x-ray reflection interface microscopy (XRIM) techniques have been used to directly probe the radiation-stimulated dissolution of calcite as shown in Figure 8. The development of corrosion-resistant experimental chambers that can also work at high temperatures and pressures is necessary, and some have been developed (Figure 9). These corrosion-resistant in situ and operando sample environments allow measurement using many spectroscopic and scattering probes under realistic operating conditions.

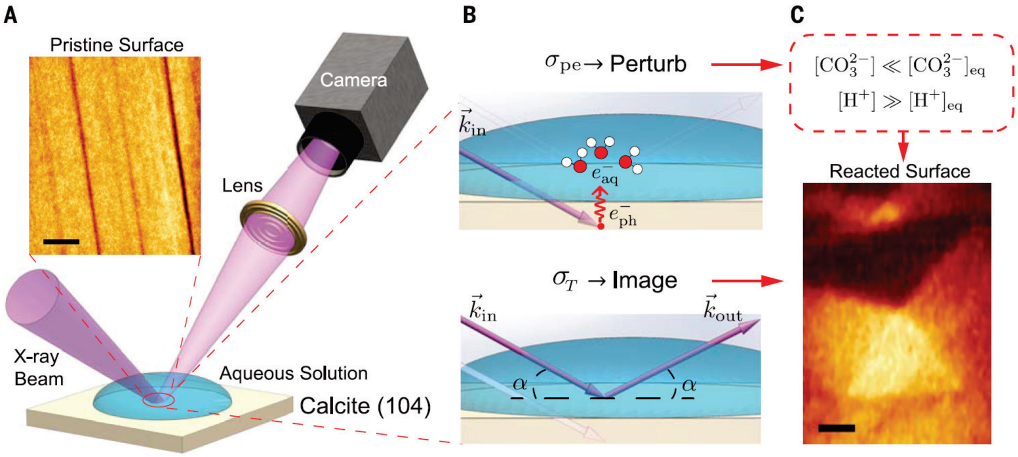


Figure 8. X-ray imaging of radiation-stimulated calcite dissolution. | From N. Laanaitet al. 2015. X-ray–driven reaction front dynamics at calcite-water interfaces, *Science* 349(6254), 1330–1334. Reprinted with permission from AAAS

A wide variety of experimental microscopic, surface science, and radiolysis techniques have been developed in recent years and have been applied to elucidate the mechanistic detail of interactions and processes at solid/liquid and solid/solid interfaces pertinent to water-based reactors. This huge array of sophisticated methodologies can now be applied to the solid/fluid and solid/solid interfaces under stimuli relevant to next-generation nuclear reactors.

Experimental advances must be accompanied by theoretical developments to establish the comprehensive understanding needed for implementing future reactor systems. Developing multiscale, integrated models for complex interfacial processes is required. New computational tools (electronic structure, embedded methods, multiscale simulations, and machine learning) can lead to mechanism-based design of materials and interfaces. Development of an integrated mechanistic model is required for the design of complementary and compatible reactor materials and coolants.

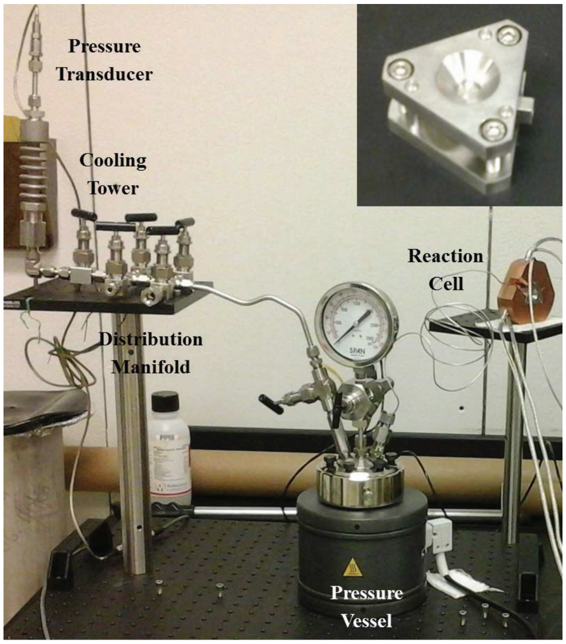


Figure 9. Corrosion-resistant apparatus for high-pressure and high-temperature x-ray studies. | Reproducted from M. S. Elbakhshwan et al. 2016. "Sample environment for in situ synchrotron corrosion studies of materials in extreme environments," *Rev. Sci. Instrum*. 87, 105122, with permission of AIP Publishing

Understanding corrosion under radiation, stress, and high temperature

Whereas corrosion has been studied for decades, much of the reported work tends toward empirical observations, is very system specific, or focuses on a limited microstructural component of the corrosion process. Thus, while much has been learned, there is not a unifying scientific foundation that ties together the nonequilibrium kinetics and thermodynamics of moving interfaces and atomic motion—the local microstructural, morphological, and physical features, as well as the environmental effects that influence the collective corrosion response from the earliest interactions through a decades-long processes. The priority for future research thus needs to tie together an understanding of the following:

- The free energy or kinetic rates that lead to structural changes associated with oxidation or dissolution. We call these the ***drivers*** of corrosion.
- The local microstructural features and the local compositional changes or fluctuations that establish the local free energy or kinetic rates. Since any system undergoing corrosion quickly moves away from homogeneity, this local variability can trigger very different responses than would be expected from a homogeneous system. We thus call these ***triggers*** for corrosion.
- Changes to the environment of the material being corroded, or to the fluid causing the corrosion, can dramatically change the corrosion response. These changes could include radiation that changes material microstructures or rates of atomic diffusion. They could also include radiation or impurities in the coolant that change the coolant–metal interaction rates. In every case, the pathways for corrosion are strongly dependent on these environments. We thus call these corrosion changes ***dependencies***.
- The chemical reactions and/or the collective motion of atoms that takes place, given the drivers, triggers, and dependencies. Since this collective motion of atoms defines the progression of the overall corrosion response, we call these collective motions the ***mechanisms*** of corrosion.

The ultimate goal would be to develop a set of scientific principles, valid across multiple material systems, that allow prediction of corrosion paths and therefore mechanisms. These principles would include the knowledge necessary to design specific chemistries and microstructures for control of mechanisms such that the material forms thin, stable, protective surface layers. To reach the grand vision of controlling corrosion in any specific environment (dependencies), it is critical to make systematic advances in understanding corrosion-controlling processes (the drivers and triggers and their interplay) at multiple scales. The discovery process would work from understanding corrosion in idealized systems; to understanding how the presence and/or addition of defects changes corrosion pathways; to understanding how external stressors like radiation, mechanical stress, or environmental impurities alter the corrosion response. Although the emphasis here is on corrosion-related failure, it is necessary to understand how stress, temperature, and irradiation impact the deformation processes and the mechanical response, as these may trigger alternate failure mechanisms.

Idealized systems

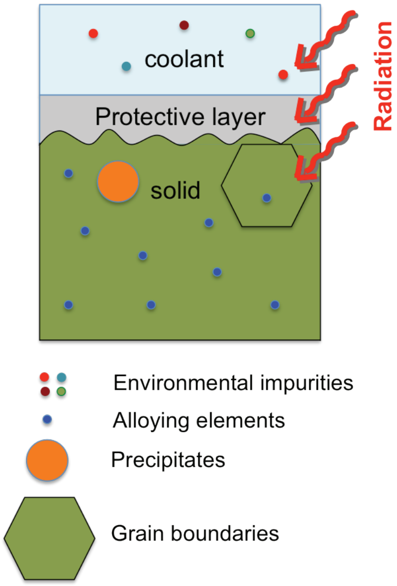


Figure 10. A schematic representation of a corroding system, including a solid material, a protective layer, and a coolant. An idealized system consists simply of a coolant, a solid, and potentially a protective layer. Realistic (defected) systems include heterogeneities, such as alloying elements, second-phase precipitates, surface roughness, and grain boundaries. In extreme environments of nuclear reactors, one also needs to account for the external stressors, such as radiation and environmental impurities.
| Image courtesy of I. Szlufarska, University of Wisconsin–Madison

Idealized systems should be understood first before moving on to complex systems with defects and external effects. As discussed in Figure 10, an idealized system refers to the simplified model of a coolant, a protective film, and the solid, in which each of these three components is chemically and structurally homogeneous. In these systems, it is important to understand the nonequilibrium thermodynamic and kinetics of the moving interfaces, including the balance of dissolution and regrowth. Key issues include the drivers that control whether the interfaces are flat, are complex in three dimensions or perhaps oscillate with time, and how these couple to the dependencies, such as the coolant in a reactor. The fundamental processes that lead to delamination and failure of protective oxide films are still controversial in the current scientific literature, an issue that needs to be resolved. For instance, what are the relative roles of destabilizing drivers—such as stresses in a protective oxide film due to electromechanical issues such as high electric fields, misfit at the interface to the metal, and deformation processes—in relation to the roles of triggers for delamination, such as voids in the oxide, the metal, or the interface? While these phenomena matter for the substrate material, they also will lead to the presence of impurities and nanoparticles in the coolant liquid, which leads to other concerns. These are issues for which the revolutionary advances in characterization and modeling tools made over the last decade offer the opportunity for key scientific breakthroughs that will facilitate significant improvement in future nuclear materials.

Defected systems

Although much fundamental understanding of oxidation and corrosion can be achieved by investigating pure metal systems, it is crucially important to extend this understanding to multicomponent alloys and to determine the roles of structural and chemical heterogeneities (see Figure 10). These multicomponent alloys are typically thermomechanically processed with the goal of achieving optimized microstructures that improve the initial properties of the metal (e.g., yield strength) and its corrosion resistance. However, the irradiation continuously modifies the composition and structure of the metal, requiring an understanding of how these changes modify the mechanical integrity and the corrosion response.

Many details of how alloying elements change corrosion are scientifically ambiguous, despite enormous advances in the empirical development of alloys that show improved resistance in selected cases. At the level of simple solid solutions of trace elements, it remains unclear what are the relative roles of changes in the lattice parameters and hence interfacial stresses, surface segregation, or electronic phenomena such as dopant-induced states in protective oxide films. There is clear evidence that even small levels of metals such as molybdenum drastically change the corrosion of systems involving chromium oxide protective layers, [Morco et al 2016; Morco et al. 2017] but the underlying science is not fully understood.

Extending understanding to real materials with grain boundaries, dislocations, and second-phase precipitates involves further complications and poses further scientific questions. Microstructural features of the alloys, such as grain size, texture, and grain boundary character distribution, can dramatically affect the mechanical properties and the corrosion mechanism; and these must be understood on a fundamental level. For example, the early stages of oxidation are often associated with internal oxidation, via which oxygen diffuses along the grain boundaries of the alloys, oxidizing these internal surfaces. Although the thickness of the internally oxidized layer represents wasted thickness, the phenomenon of internal oxidation can anchor the overlying protective oxide layer, rendering it mechanically more stable. Grain boundaries represent high-energy sites in the alloy, and improper heat treatment can lead to sensitization, [NRC 2011] which can cause phases that more readily corrode to form at grain boundaries, or protective elements such as chromium to precipitate out. More recent studies have shown that grain boundary type or character can profoundly affect corrosion; in steels, low-energy grain boundaries are typically less prone to corrosion than their high-energy counterparts, providing a powerful tool to control corrosion in an alloy. All of these phenomena need to be coupled to the underlying science of the thermodynamics and kinetics of corrosion, connecting the complex behavior of engineered alloys back to the idealized systems and to the relevant drivers, triggers, mechanisms, and dependencies.

External effects in corrosion

In nuclear reactors, materials are subjected to external stressors (dependencies) that include radiation, mechanical stress, and environmental impurities—all of which can affect the degradation of the coolant and the metal. In particular, radiation effects are particular to the environments of nuclear reactors, and they lead to phenomena that do not occur otherwise. These phenomena range from radiation-enhanced diffusion in the solid material to radiolytic desorption of oxygen from protective oxides into the coolant, and radiolytic enhanced diffusion (Figure 11). Although we already understand some of the consequences of radiation in the solid, there are still too many unknowns. The effects of external stressors can also couple to one another, as in the case of irradiation-assisted stress corrosion cracking, [Hoffman et al.] and are almost certainly important for other failure mechanisms such as fretting-assisted corrosion.

Radiation effects in the coolant can also be significant, and they can couple to the corrosion mechanisms in the base solid. Specifically, the solvation properties and redox properties of the solution affect the kinetics of the individual processes involved in corrosion, and they impact corrosion pathways. Radiolysis produces redox-active species, which in turn can alter corrosion mechanisms. The effects of radiolysis on corrosion varies depending on the physical/chemical properties of the solution, and the coupling of all these phenomena needs to be understood.

In summary, there is already empirical evidence that the development of protective oxide films can be drastically different with and without radiation, but our understanding of the science underpinning these processes is incomplete.

Opportunities

To address the aforementioned scientific challenges, it will be necessary to develop and adopt state-of-the-art theoretical, modeling, and experimental tools in an integrated fashion. On the theory and modeling side, the goal is to develop predictive models that are based on an understanding of thermodynamic and kinetic drivers, as well as of mechanisms and triggers, that control materials degradation in the coupled extreme environments (dependencies) of nuclear reactors. In addition, modern techniques, such as data mining and machine learning algorithms, provide a new exciting opportunity to learn from historical as well as new data to predict systems (e.g., alloy or coolant compositions) that have superior corrosion resistance. A significant opportunity to unravel the synergistic effects of extreme environments is the development of in situ techniques that allow for coupling of the effects of radiation, environments (i.e., controlled chemistry and temperature) and nanoscale characterization in a single experiment.

Potential Impacts on Energy Technologies

Enhancing the properties of surfaces under harsh conditions will lead to increased and improved interfacial performance that extends across DOE, from reactors to waste storage. Radiation and interfaces are ubiquitous in the nuclear power industry, and processes initiated at interfaces are responsible for subsequent corrosion and failure of components. The need for understanding and controlling processes occurring at interfaces is wide ranging and of vital importance.

Success in advancing the fundamental knowledge of the processes occurring at interfaces exposed to high radiation fields, temperature, and pressure will lead to improved safety and stability of the current reactor fleet by increasing safety margins in, for instance, loss-of-coolant accidents. Reduced corrosion and erosion of materials will be obtained, as well as the decreased transport and deposition of activity within gas, liquid metal, and molten salt reactor systems. Expected advances from this research will lead to fuels and cladding materials better able to withstand higher burnup, higher temperature gradients, and other hazards associated with the next fleet of nuclear reactors, as well as increased lifetimes of advanced reactor systems.

Absent the burden of radiation, similar performance challenges exist in the use of molten salts, ionic liquids, and other fluids employed in heat transfer systems. For example, the understanding of high-temperature interfacial chemistry and corrosion processes obtained in the context of nuclear applications will be equally valuable for the deployment of durable and reliable systems for thermal conversion of solar energy.

PRD 4: Reveal Multiscale Evolution of Spatial and Temporal Processes for Coupled Extreme Environments

***Key question**: How can computational and experimental techniques be integrated to bridge spatial, temporal, and energy scales that underpin materials' behavior and chemical transformations in coupled extreme environments?*

The materials used as fuels, coolants, and structural components in advanced nuclear reactors are exposed to multiple extreme external stimuli, e.g., temperature, stress, pressure, environment, and radiation. Each of these external stimuli independently has the potential to degrade the properties and performance of the material; when they are coupled synergistically, the degradation processes may be modified or accelerated. The continuous evolution of the intrinsic properties of the fuel, coolant, and structural materials induced by these external stimuli introduces additional variables that add to the complexity of identifying, understanding, and designing against the degradation processes. For example, the presence of the fuel dissolved in a molten salt complicates the corrosion processes. In the fluid at the interface with the structural material, radiation-induced ballistic collisions with the salt can change near-surface salt chemistry, which changes the local driving forces for dissolution. Additionally, the salt chemistry constantly changes with irradiation, adding new elements to the salt and thus changing corrosion potentials.

The time scale on which reactions can occur is as short as 0.1 femtosecond, but these initial events can trigger degradation mechanisms on time scales of months and years, with ultimate failure occurring in decades. Understanding the reactions also requires a multiscale approach that extends from angstroms to meters; see the sidebar "Corrosion from the Atomistic to the Continuum Level" for an example. To address the scientific challenges associated with determining performance degradation issues under changing external and internal variables will require advances in computational and experimental methodologies and forging of a new and stronger integration between them. Each will have to become multiscale within itself and integration between them attained. The experiments will need to be conducted in real time while the material is exposed concurrently to high temperatures, pressures/stresses, and/or radiation fluxes. This PRD recognizes the need for multiscale, multi-method approaches to identify the degradation processes that will operate in the coupled extreme environments envisioned for advanced nuclear systems.

Scientific Challenges and Opportunities

This PRD seeks to discover the fundamental changes in the properties of fuels, coolants, and structural materials that occur over spatial and temporal scales spanning multiple decades. They occur as a result of the coupled extreme environments that can act independently or in concert to degrade the properties and performance of the materials. A key scientific challenge is that the systems under investigation and the external variables themselves are not static but continually evolving. That is, determining the degradation of a material requires that the degradation in properties and responses be determined not only in pristine materials but also in various degraded states. Furthermore, the degradation processes themselves occur over the operational lifetime, and they are likely to be modified as the fuel, coolant, and structural material evolve. Since these are time-dependent processes, there is also a need to assess processes and mechanisms in environments that mimic the operational conditions, and to be able to do so over a wide range of spatial and temporal scales.

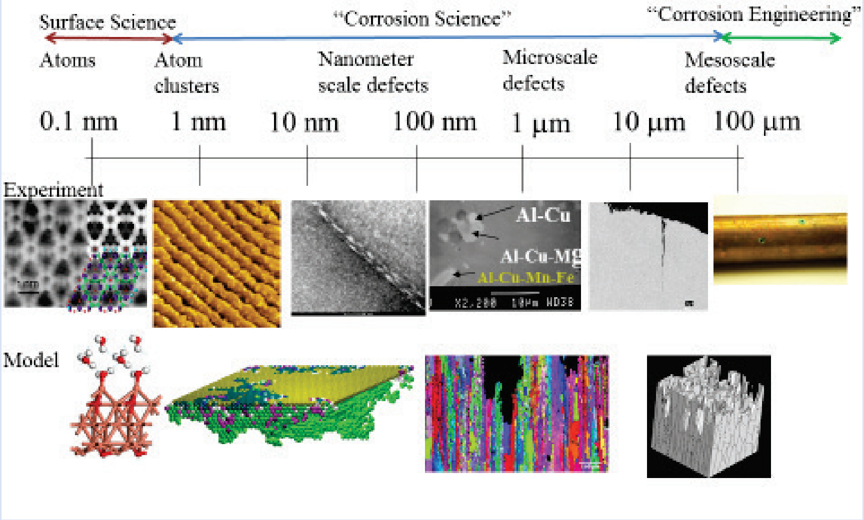
Thus the following are key scientific challenges to be addressed:

- How are the intrinsic properties of the fuel, coolant, and structural materials modified by the extreme environments found in advanced nuclear reactors? For example, can we determine how exposure to the irradiation environment over the operational lifetime affects the physical and chemical properties of the coolant?

- What is the impact of exposure to coupled extreme environments on the spatial and temporal dependencies of the key degradation processes and mechanisms? For example, what are the relationships between the physical and chemical properties of the coolant and the attendant corrosion processes and mechanisms?

Corrosion from the Atomistic to the Continuum Level

Corrosion is a multi-spatial and multi-temporal problem. The spatial range varies from initiation events at the atomic level through nanometer-scale defects in materials that then migrate and cluster to create larger defects, eventually leading to failure over a long time scale under the influence of stress and environment. Processes at multiple length scales dictate both corrosion susceptibilities and modes of attack, as well as how a surface layer regulates these processes to provide protection. To understand these processes requires study at the resolution limits of existing experimental methods in order to understand the mechanisms necessary to guide improvements in materials design.



From a computational viewpoint, the atomic structure and surface morphology of a homogenous region can be modeled by density functional theory and Monte Carlo methods (lower left). Although this information provides some insights into mechanisms, major scientific challenges are to advance the ability to investigate the complexity of materials that will be deployed as structural materials in advanced reactors, and to introduce and explore the relevant complex structures. Furthermore, it is essential that computational methods evolve to explore the roles of microstructural heterogeneities, grain boundary nano-chemistry and structure at the 1–1000 nm scale, and grain texture that often governs corrosion. | Images courtesy of Oak Ridge National Laboratory, Pacific Northwest National Laboratory, and University of Michigan

To address these scientific challenges, the following research thrusts were identified. These seek to reveal the multiscale evolution of spatial and temporal processes that operate in coupled extreme environments and lead to degradation in the desired property of a material. The research thrusts recognize the need to conduct in situ, operando experiments with multi-modal diagnostic capabilities to assess the fundamental mechanisms and processes. These experiments cannot be conducted in isolation but must be fully integrated with advanced computational methods.

Discovery of multiscale processes that lead to degradation of coolants and structural materials

Experimental framework

Through advances in scattering, spectroscopy, and electrochemical techniques, it is now possible to employ simultaneously a variety of diagnostic tools to uncover the physical and chemical processes that govern the degradation in performance of material systems over different spatial and temporal scales. The information gained at one spatial and temporal scale informs the interpretation of the data at successive spatial and temporal scales, until ultimately a comprehensive understanding is achieved of the processes and mechanisms at the atomic and molecular scales, though the mesoscale, to the continuum scale. Three-dimensional data sets can now be garnered to provide a snapshot in time of the reaction kinetics, bringing closer the concept of coupling 3D spatial data with temporal information. Moreover, and important to answering the challenges relevant to advanced nuclear systems, experimental capabilities have been or are being developed to enable the experiments to be conducted in real time and under environmental conditions that duplicate or replicate the application environments. If these approaches include multiple in situ diagnostic capabilities—coupled modality capabilities—they can provide information on the reaction kinetics over a range of temporal and spatial scales under actual operational environments.

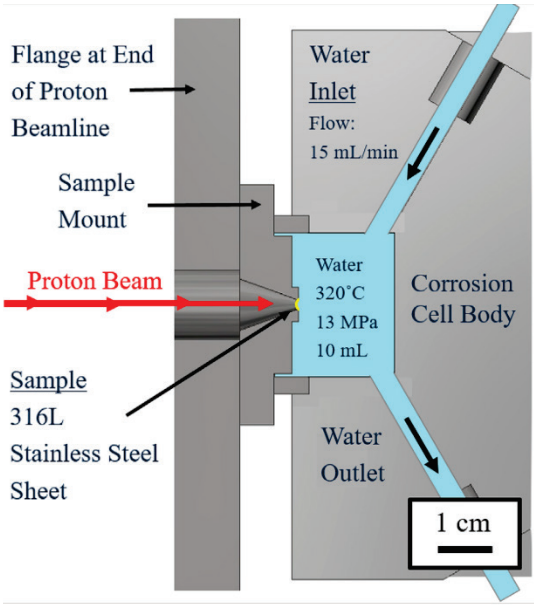


Figure 11. Proton beam irradiation of 316L stainless steel while exposed to high-temperature water with added hydrogen to study the effect of radiation on corrosion. | Reprinted from *J. Nucl. Mater*. 493, S. S. Raiman and G. S. Was, Accelerated corrosion and oxide dissolution in 316L stainless steel irradiated in situ in high temperature water, 207–218, copyright 2017, with permission from Elsevier

For example, it is now feasible to monitor in situ the corrosion of a metal exposed to a high-temperature liquid metal or aqueous environment under simultaneous irradiation. Figure 11 provides an example of such an experimental station. [Raiman and Was 2017] Using this approach, it was shown that the irradiation of 316L austenitic stainless steel in water with an added hydrogen environment resulted in the formation of a thinner and more porous oxide with a lower chromium content than in the unirradiated material. [Raiman and Was 2017] This difference was attributed, following post-corrosion characterization, to the dissolution of chromium-rich spinel oxides in irradiated water, leading to an accelerated rate of inner oxide dissolution. The results further suggested that a pre-formed protective oxide may be effective in preventing chromium loss in irradiated water. Similarly, lead bismuth eutectic produced a less dense and more porous oxide on HT9 in the presence of irradiation. [Frazer et al. 2016] These results show the potential of building experimental instruments and developing techniques to enable real-time monitoring and in situ characterization in which the material of interest is subjected to multiple external stimuli simultaneously. In this case, in situ diagnostic capabilities need to be developed to provide insight into the reaction kinetics not achievable from post-reaction characterization.

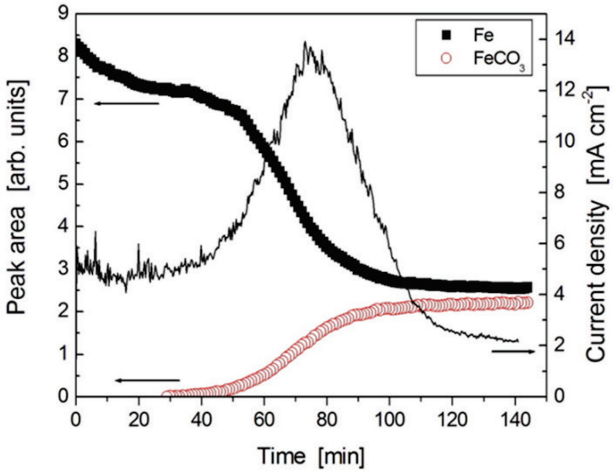


Figure 12. Plot of current density (light line) during siderite growth on iron as monitored by in situ x ray diffraction (heavy lines). | Reproduced from B. Ingham et al., 2015, First stages of siderite crystallisation during CO_2 corrosion of steel evaluated using in situ synchrotron small- and wide-angle x-ray scattering, *Faraday Discuss*. 180(0), 171–190, with permission of The Royal Society of Chemistry

The production of crystalline oxide phases during corrosion may or may not produce protective layers, and failures in the oxide phase may result in localized corrosion. Understanding the nucleation of oxide phases requires knowledge of precursor states and the growth of these nuclei over a wide temporal and spatial range. For example, Ingham et al. used in situ synchrotron small- and wide-angle x-ray scattering to determine the oxidation of steel exposed to a CO_2-saturated brine solution. They observed the initial formation of amorphous nanoparticle iron carbonates and their evolution over time into nucleation sites and crystal formation of $FeCO_3$ (sederite). [Ingham et al. 2015] Current density was observed with the onset of nucleation, and it dropped again as protective oxide formation occurred (Figure 12). Coupled modality characterization techniques such as this have the capability to elucidate reaction mechanisms that occur over a range of siderite particle sizes on a solution interface. However, the combination of methods required likely differs depending on whether the coolant allows passivation and the subsequent mode of corrosive attack. Adding the ability to add simultaneous temperature, radiation, or loading would extend the capabilities of such an experimental method to address degradation mechanisms applicable to advanced nuclear reactors.

Computational framework

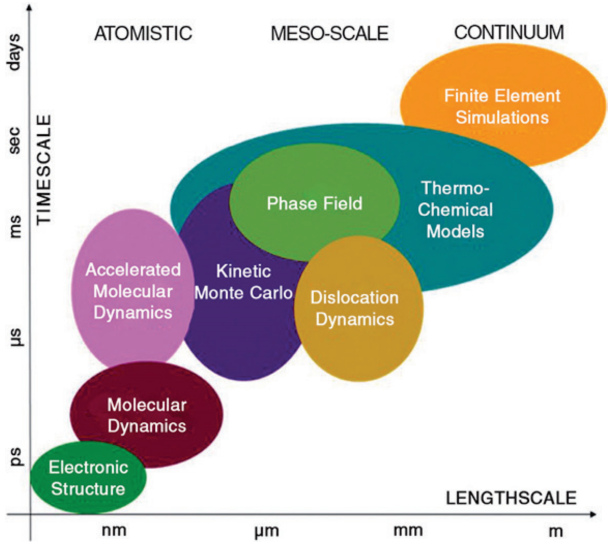


Figure 13. The time and length scales appropriate to different calculation modalities. | Reprinted from *Mater. Today* 12(11), M. Stan, Discovery and design of nuclear fuels, 20–28, copyright 2009, with permission from Elsevier

In addition to adopting a multiscale experimental approach, there is a pressing need to bridge the spatial and temporal scales computationally. Figure 13 shows the time and length scales appropriate to the different calculations. [Stan 2009] Bridging these scales will require combining the accuracy and flexibility of electronic structure calculations with the speed of classical potentials by merging and exploiting the best insights from the fields of machine learning, advanced optimization, and atomistic simulations. Model machine learning algorithms, such as deep learning and genetic algorithms, are needed for the enhanced sampling of training data with experimental inputs. There is a need to leverage state-of-the-art advances in model-building algorithms, such as genetic algorithms, compressive sensing, and deep neural networks, to describe scenarios that deviate far from equilibrium. Yet to leverage these advanced intelligent learning approaches requires experimental and theoretical data that reveal the essential phenomenological patterns that then enable predictive capability. At present, a single framework encompassing such information across multiple length and time scales is lacking; this remains a scientific challenge. A second key scientific challenge for the computational community is to advance from idealized surfaces and systems to address ones with heterogeneities on the surface and in the bulk, including those that develop as the materials evolve under irradiation; and to develop the computational capabilities that explore the spatial scale of relevance to the degradation mechanism. This challenge includes developing potentials that account appropriately for magnetic effects, impurities, precipitates, and so on.

Development of an integrated framework

While the multiscale experimental and computational approaches present significant challenges in their own domain, another major challenge is the synergistic coupling of experimental and computational methods across all relevant spatial and temporal scales. This must be met to address the loss in performance of materials used in complex and multi-component harsh environments.

An example of the insight into fundamental processes that can be obtained by coupling theory and experiment is provided by the recent studies of radiation damage evolution in equimolar metallic alloys, including those that contain five or more elements—often referred to as "high-entropy" alloys. The enhanced properties of these concentrated solid-solution alloys are attributed to a combination of thermodynamic and kinetic effects, the local lattice distortions, and to the combined effect of the intrinsic properties of the elements. The ab initio Korringa–Kohn–Rostoker coherent-potential-approximation method—which was implemented within density functional theory (DFT)—provided insight into the variation in the density of states as the number of elements increased in the nickel-based alloy series formed with Cr, Co, Mn, Fe, and Pd additions. [Zhang et al. 2015; Zhang et al. 2017] The results showed a substantial decrease in the electron mean free path, which impacts how heat is transported away from the displacement cascade. The electrical and thermal conductivity were predicted and experimentally shown to be significantly lower in the more complex alloys than in pure nickel. Molecular dynamics (MD) computer simulations showed that the defect migration and formation barriers were higher in the binary alloys than in nickel, and that the production of extended defects was related to the collision and not the ballistic phase of the displacement cascade. [Beland et al. 2016] Together, these results suggest that the radiation resistance of these alloys should increase with increasing alloy complexity. In general terms, this prediction has been substantiated by several different experiments, although it has emerged that a specific element can play a more significant role than the number of elements. [Zhang et al. 2015; Lu et al. 2016] The theoretical and computer simulations clearly provided an interpretation of the experimental results in terms of intrinsic properties not accessible in the irradiation experiments. It now remains to create enough information about the patterns of behavior associated with alloy series to train learning algorithms and enable the capability to predict materials properties in more-complex, higher-component materials.

A second example demonstrates that new experimental approaches are needed to understand the predictions of calculations of material degradation processes. Much is known from first-principles calculations about how electroactive ions diffuse through a lattice, [Van der Ven et al. 2013] but little is known experimentally about the atomic-scale processes involved in ion diffusion. The ability to characterize such phenomena over the length and time scales required for comparison with theory has until now been limited by the available experimental tools. This has in turn restricted the ability to develop validated design guidelines to manage ion diffusion in materials. The capabilities of free electron x-ray lasers may enable much more detailed insight into ion and atom migration in complex materials under operating conditions. For example, x-ray photon correlation spectroscopy has already been shown to be a powerful probe of atomic diffusion, [Leitner et al. 2009] but it is currently limited to relatively slow time scales (>ms). Advanced high-flux x-ray photon correlation spectroscopy with high-repetition-rate free electron lasers has the potential to enable studies of ion diffusion at high spatial resolution. [Carnis et al. 2014]

Development of an integrated computational and experimental framework to understand environment-assisted cracking

Understanding uniform modes of corrosion requires understanding transport rates, interface reaction mechanisms, and rate-controlling processes. These phenomena depend on the coolant and coolant/fuel hybrids being considered. The challenge will be to address the modes of corrosive damage that combine several external stimuli with material transformations driven by related factors. The combination of factors gives concern regarding sophisticated modes of corrosion such as local microstructural attack, de-alloying, and environment-assisted cracking (EAC).

Dissolution of structural materials is a key factor in heavy liquid metals based on Pb, Bi, and Sn and light liquid metals such as Na or Li. Although the dissolution can be mitigated by purposely doping the liquid metal with passivating elements such as oxygen, the detailed understanding of the transport of elements through these interfaces is not fully understood. The complexity of the challenge is magnified because these phenomena are accompanied by microstructural effects such as de-alloying and associated phase transformations, multiple layers of different oxide types, and porosity, making a temporally and spatially accurate description of the phenomena difficult. For sodium and lithium, the degradation is attributed to the impurities in the liquids. Again, it is the transport of specific metal species to the surface that governs the progress of the phenomena and controls the impurities; therefore, the chemical reactions are challenging and need to be addressed in a fundamental fashion.

Salt-cooled systems will operate at temperatures above 600°C. These systems exemplify an environment in which materials must perform in the coupled extreme environments of high temperature and radiation. The corrosion itself is a competition of thermodynamic drivers at the corrosion front and kinetic processes as atoms diffuse in response to reactions at the fluid/metal interface. Additionally, the radiation-induced changes in the microstructure and, more important, in the composition of the salt, influence the competition between thermodynamics and kinetics of the corrosion reactions. The high temperature leads to corrosion, specifically dissolution of alloying elements such as chromium from structural materials into the salts, which reduces the free energy of the system (Figure 14). [Lister 2012] The dissolution is faster at grain boundaries, which act as fast pathways for chromium to reach the surface. Under radiation, the grain boundary composition changes as a result of radiation-induced depletion of chromium at the boundary. [Bruemmer et al. 1999] Nominally, this reduction of chromium at the grain boundaries will slow down the loss of chromium to the salt, but the complexity of these competing nonequilibrium processes remains to be understood.

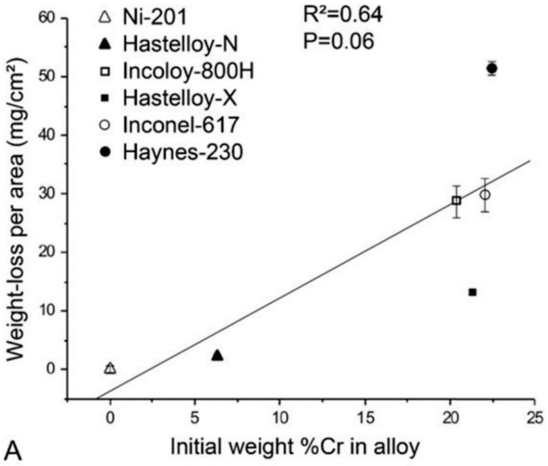


Figure 14. Correlation between chromium content in the alloys and weight loss due to corrosion. Samples from nickel-based alloys were exposed to FLiNaK salt at 850°C for 500 hours. | Reprinted from *Molten Salt Chemistry: From Lab to Applications*, eds. F. Lantelme and H. Groult, K. Sridharan and T. R. Allen, "Corrosion in Molten Salts, 241–267, Elsevier, Oxford, copyright 2013, with permission from Elsevier

Identifying how the coupling of multiple external stimuli expands or contracts the susceptibility window for EAC

EAC of a particular metallic system occurs when there is a critical combination of chemical, electrochemical, and mechanical factors that, when coupled, render a material susceptible. These factors produce crack initiation and growth that likely would not occur in the absence of any one of these factors. The operating temperature, the coolant and fuel, the pressure, and the radiation constantly modify the coolant, fuel, and the intrinsic properties of the structural material and the surface state, which will enable or accelerate interfacial reactions. The key scientific challenge will be to identify—through the synergistic coupling of multiscale experimental and computational approaches—the chemical, electrochemical, and mechanical driving forces; the dependencies on the evolving material condition; and the mechanisms behind crack initiation and propagation in the bulk and at specific sites. That is, the key challenge is not only to define how the coupling of extreme environments modifies the susceptibility window for EAC but also to uncover the fundamental mechanisms that govern the change.

Liquid metal embrittlement, for example, is a specific form of EAC in which bare metal-to-metal contact occurs. Although liquid metal embrittlement is a commonly observed phenomenon in systems such as Ga/Al, Hg/Al, Pb/ferritic steel, and many others, many aspects remain unknown—such as the intrinsic and extrinsic drivers and dependencies of this phenomenon. For example, if the introduction of impurity species into the grain boundary is insufficient to cause it to fail, as some DFT calculations have suggested, what are the other forces driving embrittlement? Is the change in the grain boundary structure due to the introduction of the impurity the additional driving force [Luo et al. 2011]? Is the plastic deformation and its attendant impact on the grain boundary an additional driving force [Gorse et al. 2011]? The scientific challenge is to uncover these driving forces and determine how they are modified by the continuously evolving structural material and external variables.

Potential Impacts

Successfully meeting the challenges outlined will enable a deeper fundamental scientific understanding of the evolution of material properties and performance under exposure to stress, temperature, corrosive environment, and radiation. This understanding will be achieved by coupling new, multi-modal measurement techniques integrated with theory and modeling. The impact will be an improvement of system operating lifetimes that leverage initial capital investments in plant construction; improved energy generation efficiency through improved heat transfer resulting from decreased degradation of fuel cladding/coolant interfaces; and the resultant improved safety that arises from more durable, dependable materials in both primary and support plant systems. It can be reasonably imagined that new tools and deeper understanding will have important impacts on other energy systems as well, including new materials for renewable energy technologies, such as concentrated solar power; for energy storage technology, such as advanced batteries; and for the transport of energy from source to load locations. Finally, strategies for designing new materials tailored for specific applications will emerge based upon this new knowledge, perhaps even taking advantage of synthesis under the extreme conditions under which these reactors will operate.

PRD 5: Identify and Control Unexpected Behaviors from Rare Events and Cascading Processes

***Key question**: How do we identify, anticipate, and control rare events that initiate cascading processes and cause aberrant properties and materials' responses?*

The extreme conditions associated with nuclear energy systems emphasize the importance of understanding processes that can be controlled by multiple factors. One such factor is so-called rare events that are characterized by vastly different time scales of the event, the accumulation of those processes, and the eventual outcome in the context of system reactivity or behavior. Other important factors include unpredictable stochastic processes, and minority species (e.g., defects, impurities) whose reactivity or physical properties impact the system inordinately. Many phenomena depend in a nonlinear fashion on differences in structure; the distributions of defects and impurities; or even the fluctuations in energy, properties, or organization, rather than the average. Fluctuations can adopt dramatically different behavior depending upon the extreme conditions within nuclear energy systems, leading to unanticipated reaction pathways. A robust, validated mechanistic knowledge of material and chemical processes at the time and length scales of the controlling events and interactions is needed to attain a predictive understanding of the role of high-impact/low-frequency processes that can lead to unexpected reactivity or materials degradation, including catastrophic failures. The need to understand the controlling events associated with singular processes is a major challenge for experimental, computational, and theoretical approaches.

Scientific Challenges and Opportunities

The exposure of materials to extreme chemical and physical perturbations can lead to unexpected behaviors that are challenging to anticipate, predict, and control. (See the sidebar "Unexpected Sensitivity of bcc Alloys to Radiation Damage.") Under such circumstances, an understanding of the average properties of a system responding to such perturbations—for example, through the ensemble integration of stochastic processes—is not sufficient. Rather, it is necessary to obtain a more robust understanding of the wide array of materials processes that occur, including

> *"A new type of energy science can be developed to understand real materials under real-world conditions, including even the slow and statistically rare events that can dictate success or failure of materials."*
>
> From Hemminger 2015, p. 20

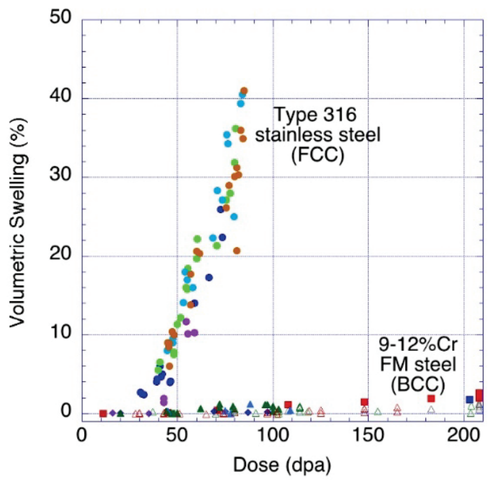
- Incorporating the role of rare (low-probability) events and the associated variability in behavior, such as including deviations from Gaussian statistics or an ensemble average that is not well formed
- Understanding how the manifestation of processes can change across length and time scales, such as connecting atomic-, nano-, meso- and eventually macro-scale processes
- Assessing the role of minority, often trace, components, such as defects and impurities

In some cases, seemingly identical structures can react in distinctly different fashions. Detecting and probing these phenomena at the appropriate length and time scales—through experimental, computational, and theoretical approaches—is a major scientific barrier that has been identified as a key element in a transformative research agenda (e.g., in the DOE BES report *Challenges at the Frontier of Matter and Energy* [Hemminger 2015]).

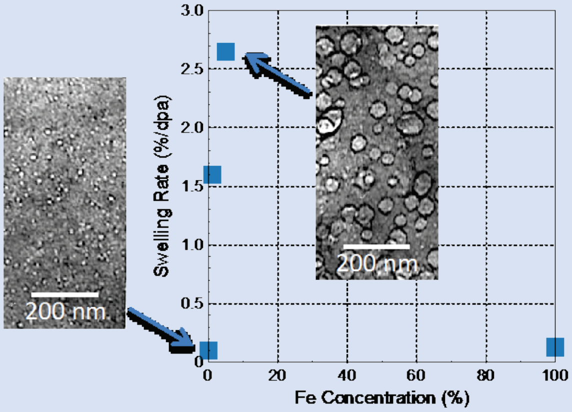
Unexpected Sensitivity of bcc Alloys to Radiation Damage

Metallic alloys based on the body-centered-cubic (bcc) crystal structure are generally observed to exhibit superior radiation tolerance compared with face-centered-cubic (fcc) alloys. For example, the radiation-induced dimensional change (volumetric void swelling) observed in austenitic (fcc) stainless steels is about an order of magnitude higher than in ferritic/martensitic (bcc) steels (upper image). Consistent with this observation, both vanadium and iron, in their elemental forms, have a bcc structure and exhibit very low void swelling rates during fast neutron irradiation. Therefore, it was quite surprising that a bcc V-5%Fe alloy showed the greatest swelling of any known metallic material, and that damage in dilute V-Fe bcc alloys showed extreme sensitivity to the concentration of iron. In these alloys, a sharp increase in the swelling rate was observed upon addition of just a small additional percentage of iron (lower image).

The swelling behavior of bcc V-Fe solid solutions directly challenges our understanding of the underlying relationships among crystal structure, composition, and radiation damage. At the same time, it presents a concrete example of how an unexpected result presents a unique window for breakthroughs in developing improved radiation-tolerant materials and greater flexibility in system design.



Swelling of fcc and bcc steels as a function of heavy ion dose in units of displacements per atom. | Reprinted from *Acta Mater.*, 61/3, S. J. Zinkle and G. S. Was, Materials challenges in nuclear energy, 735–758, copyright 2013, with permission from Elsevier.



Sensitivity of radiation damage to V-Fe BCC alloy composition. | Reprinted from *J. Nucl. Mater.*, 258–263, K. Fukumotoet al. Swelling behavior of V-Fe binary and V-Fe-Ti ternary alloys, 1431–1436, copyright 1998, with permission from Elsevier.

Therefore, this PRD is focused on the need to isolate, study, model, and predict the singular processes that ultimately may control materials behavior. This is a daunting challenge, as there can be multiple layers of events masking the underlying controlling phenomena. To address these key issues, the following research challenges have been defined:

- Predicting unexpected responses to radiation exposure
- Elucidating fluctuations and defect evolution
- Revealing the origin of irradiation-assisted stress corrosion cracking
- Understanding impurity-controlled materials behavior in molten salts

An illustrative, but far from complete, set of research directions is provided herein that delineate unexpected behaviors controlled by rare events (usually unknown), minority species, and/or cascading (nonlinear) processes that are relevant to future nuclear energy systems. Mechanistic studies of such phenomena at the appropriate length and time scales will provide the conceptual underpinnings of the relevant chemical processes and materials systems that are needed to overcome many of the technological barriers to advanced nuclear reactor operations.

Predicting unexpected responses to radiation exposure

Damage to materials by neutrons (or heavy ions) begins as an atomic displacement cascade (Figure 15). It is normally assumed that this process is additive, so that the damage can be characterized within the context of the average absorbed energy (e.g., quantified by net displacements per atom). Yet, the dramatic differences in cascade profiles for two nominally equivalent initial conditions (Figure 15) illustrate the highly variable response of a material under heavy-ion exposure and the intrinsically stochastic nature of these processes.

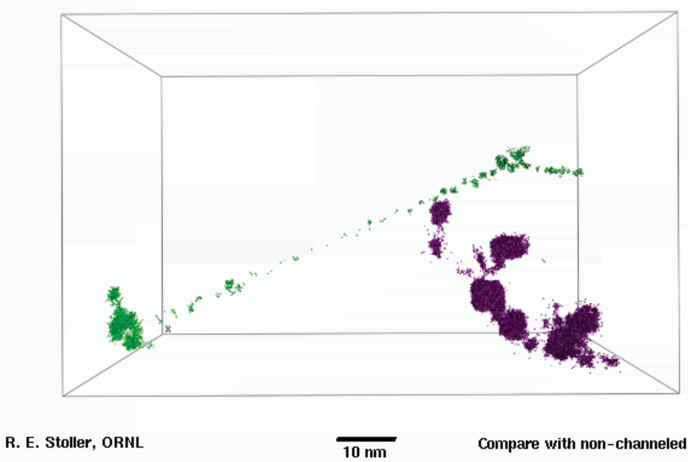


Figure 15. Comparison of defect production in two nominally equivalent high-energy displacement cascades in iron (shown separately in green and purple). | Image courtesy of R. E. Stoller, Oak Ridge National Laboratory

A dramatic breakdown of the conventional concept of linear response is demonstrated in heavy-ion damage to solids. Specifically, a significant increase in the damage cross section can occur from the interaction between the electronic energy dissipation by ions and preexisting atomic defects, as observed in single-crystal $SrTiO_3$. [Weber et al. 2015] For instance, amorphous tracks can preferentially occur in regions with preexisting defects as a result of increased thermal spikes in the damaged regions (Figure 16). That is, electronic energy dissipation through electron-lattice coupling at defects is a controlling factor in this unexpected sensitivity to ionizing radiation.

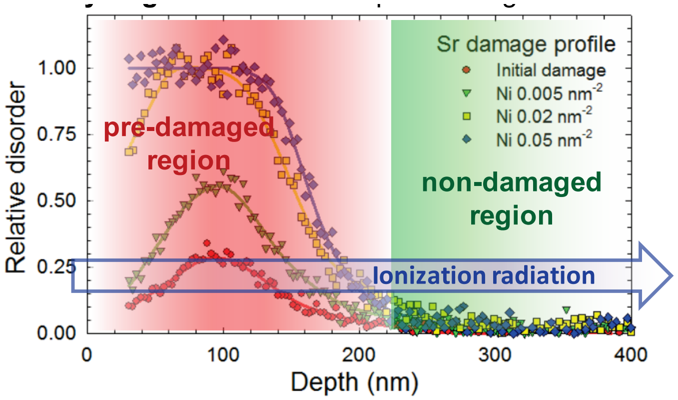


Figure 16. The synergistic effect of preexisting defects is illustrated: ionization leads to rapid amorphization in a defective region but no observable irradiation effects in a damage-free region. | Adapted from W. J. Weber et al. 2015. Synergy of elastic and inelastic energy loss on ion track formation in $SrTiO_3$, *Sci. Rep.* 5, 7726. Reprinted under terms and conditions of the Creative Commons license

Another example of deviation from the expected linear responses of materials and the critical role of preexisting defects is illustrated by controlled studies of ion irradiation of SiC, a potential fuel cladding material in future nuclear energy systems. In this case, an unexpected result of radiation exposure is the substantial annealing of preexisting defects and restoration of structural order in SiC upon ion–electron collisions. This structural healing is illustrated in a cartoon (Figure 17) showing two projected electron microscopy images of SiC. The top image shows structural disorder within a damaged crystal (smeared

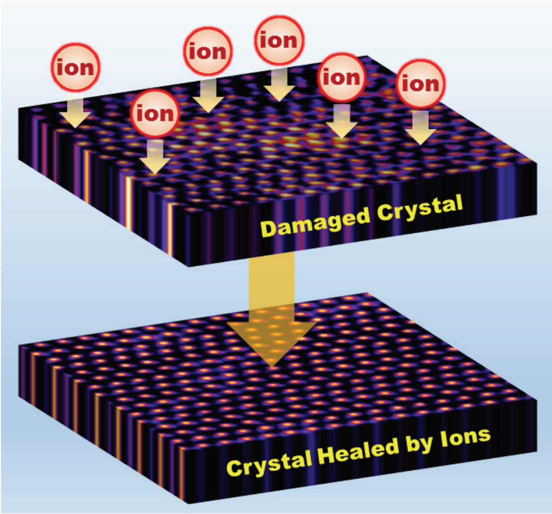


Figure 17. Bombarding a material with energetic charged particles can heal, rather than damage, the crystalline structure of SiC through local heating. | Reprinted from Y. Zhang et al. 2015. Ionization-induced annealing of pre-existing defects in silicon carbide. *Nat. Commun*. 6, 8049, under terms and conditions of the Creative Commons license.

spots in top slab), and the bottom image shows removal of damage upon exposure of the material to high-energy ions. This behavior is understood to arise from local heating of the material by energy transferred from the energetic ions to SiC electrons via inelastic ionization processes. [Zhang et al. 2015]

These examples highlight a few of the unexpected responses of materials to irradiation, especially when ionization and defect production occur simultaneously. Although self-healing processes could lead to longer-lasting components in extreme radiation environments, the distribution of the elementary damage events and the sensitivity of materials to preexisting damage represent significant challenges to the ability to predict material performance in extreme radiation environments.

Elucidating fluctuations and defect evolution

Understanding stochastic processes is critical to the design and selection of materials, particularly for ensuring the longevity of materials under extreme conditions. Materials evolution is sensitive to the kinetics of multiple competing mechanisms. A critical challenge is to go beyond a simple “mechanistic” understanding of a single event and to instead gain understanding of the entire range of events—including the outlying events that can ultimately control behavior, particularly in intense radiation environments that can result in far-from-equilibrium conditions. To achieve this understanding, new experimental and theoretical techniques are needed to probe the complex energetic landscape that the system experiences and allow the identification of the full range of outcomes that may occur, their relative probabilities, and their ultimate impact on material behavior.

An example of the challenge addressed here is manifested in the defect evolution of materials that can cascade and eventually lead to nucleation of precipitates, cracks, and voids and the coarsening of interstitial clusters. Understanding all of these is fundamental to the design of radiation-resistant materials (see the sidebar “Unexpected Sensitivity of bcc Alloys to Radiation Damage”). The stochastic variability in the evolution pathway in body-centered-cubic (bcc) iron was explored explicitly through simulations that tracked the system energy (Figure 18). These studies enabled the direct observation of a novel dislocation structure that was distinct from any previously proposed mechanisms, and they provided a direct link between experiment and simulation to aid the understanding of radiation resistance in the systems. This finding highlights the need to develop approaches that can explore the roles of controlling events within fluctuating systems.

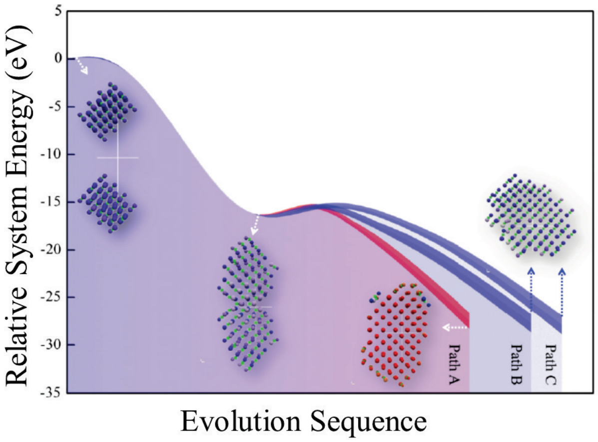


Figure 18. Multiple pathways of interstitial cluster evolution in bcc iron with comparable large transition states can exhibit substantial differences in the evolutionary path of the system. | Reprinted with permission from H. Xu et al. *Phys. Rev. Lett.*, 110, 2013. Solving the puzzle of 〈100〉 interstitial loop formation in bcc iron, 265503. Copyright 2013 by the American Physical Union.

Revealing the origin of irradiation-assisted stress corrosion cracking

Corrosion is the result of a complex suite of processes controlled by charge transfer, diffusion, temperature, and other influences (see PRD 3). Yet, in many cases, the controlling behavior is the result of the localized breakdown of a passive layer or, at high temperatures, a protective, thermally grown oxide. [Shibata and Takeyama 1976; Wu et al. 1997] Irradiation-assisted stress corrosion cracking (IASCC) is a particularly important material degradation mode for nuclear systems. For certain alloys, the susceptibility to failure by fracture due to the synergistic effects of stress in a corrosive environment is significantly enhanced in the presence of radiation damage. [Was et al. 2011] Painstaking, multifaceted experimental research and atomistic modeling have now revealed that IASCC of austenitic stainless steel in a prototypic water reactor environment is controlled by the interaction of dislocation channels (localized regions of plasticity caused by concentrated dislocation movement) with grain boundaries. [McMurtry et al. 2015] Under specific crystallographic/microstructural conditions, a dislocation channel at a grain boundary can lead to stress intensification, which ultimately can lead to crack formation. Surprisingly, when these conditions are met (identical channels intersecting the same grain boundary), corrosion cracks occur in only 18% of the cases. [McMurtry et al. 2015] This is a clear demonstration of how—despite the unraveling of complex phenomena to reveal the mechanistic underpinnings of IASCC—the underlying structural, mechanical, and/or chemical characteristics that cause dislocation channels to trigger cracking under extremes of radiation and reactivity continue to challenge our understanding of initiating events.

Understanding impurity-controlled materials behavior in molten salt

The composition of and chemistry in operating nuclear reactor fluids (e.g., a molten salt) are modified by fission product evolution, by impurities, and by the reactivity of component materials—such as the chemical dissolution of fuel, moderator, and structural materials (see PRD 1). Results from the MSRE provide several compelling examples of the sensitivity of material behavior to transient/fluctuating chemistry.

The principal constituents of the MSRE fluoride salt were LiF, BeF_2, and ThF_4, together with the UF_3 and UF_4 fuel [Ting et al. 1977] and associated fission products. Of these many components, the presence of a few minor elements (e.g., Te, Nb, ^{3}H) was particularly problematic with respect to key operational factors (such as corrosion). [Williams and Toth 2005; Ting et al. 1977] The fate of tellurium in the salt, in particular, provides an excellent example of the synergies between fuel/coolant chemistry and material compatibility. Tellurium was found to embrittle the Hastelloy N in contact with the salt, but only at higher salt oxidation potentials. Post-exposure examination showed considerably more tellurium within the grain boundaries from the oxidizing domain than from the reducing domain, with a sharp transition in embrittlement susceptibility over a narrow potential range (Figure 19). This finding demonstrates how the presence of minor constituents can exert an outsized influence over materials integrity with just small changes in a key operating parameter of the reactor fuel/coolant (i.e., the redox potential)—especially at specific defect sites where impurities and geometry can dominate local chemistry.

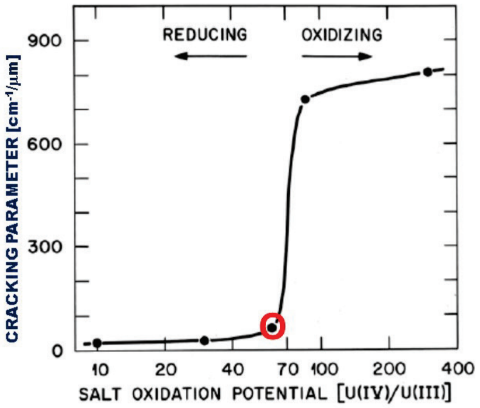


Figure 19. Influence of oxidation potential on the embrittlement of Hastelloy N in the presence of dissolved tellurium. The red circle suggests a suitable operating point at which the tellurium concentration in Li_2BeF_4 is below the threshold for severe embrittlement. | Reprinted from D. E. Williams and L. E. Toth. 2005. Chemical Considerations for the Selection of the Coolant for the Advanced High-Temperature Reactor, Oak Ridge National Laboratory Letter Report ORNL/GEN4/LTR-05-011

Most of the phenomena discussed have complex drivers related to physical and chemical processes and may depend on minor elements and/or highly localized structures. Material behaviors are often directed by coupling between chemistry and local structure on a small scale. Examples include bilayer grain boundary complexions in bismuth-doped copper and their role in embrittlement [Kundu et al. 2013] and IASCC, in which the effects of deformation and radiation on grain boundary structure are as important as those of reactions at those interfaces. By their nature, the linking of these underlying structural and chemical factors challenges our capabilities to resolve them at the appropriate length and time scales needed to identify controlling events and processes.

New characterization methods that probe how, where, and how often and/or how fast events occur are critically needed to understand the controlling aspects of stochastic processes. For example, as discussed earlier, to understand the full range of processes that occur under these extreme conditions, a suite of experimental techniques such as in situ microscopy, scattering, and spectroscopic approaches are needed that operate at different length or time scales. Ideally, these events need to be studied with simultaneous high spatial resolution and large fields of view, and in situ/operando, so rare events or very dilute species and isolated structures can be observed (as described in the Crosscutting Themes panel report). These challenges can be addressed, at least in part, by observing events that are externally triggered to analyze both the subsequent initiation and temporal evolution of changes in the system. For example, high-resolution experimental probes, such as scanning transmission electron microscopy, x-rays, and neutron diffraction, that provide atomic-scale sensitivity require the use of high-energy-density probe beams. As a result, studies conducted with these high-energy, highly focused probes may provide essential information about the role of radiation fields that will be encountered within a reactor environment, such as radiolysis of the molten salt coolant. Such studies can provide both insights into the mechanisms, and quantitative information—such as the mobility of defects, chemical fronts, and transformations—that is critical for validation of atomic-level simulations of materials and as input for longer-length-scale modeling.

The availability of new characterization tools to provide high-resolution and even dynamic information on materials systems must be coupled with new computational approaches. Data analytics tools, such as uncertainty quantification, are needed to identify key variables that affect the various chemical and physical processes. Traditional and ab initio statistical mechanics methods must be coupled to techniques that can probe the full potential energy surface, wherein the appropriate collective coordinates are used to elucidate the distributions of outcomes so that the effects of internal and external variables upon distributions can be ascertained. Nudged elastic band calculations, metadynamics, accelerated dynamics, and other approaches [Barducci et al. 2011; Henkelman et al. 2000] are critical to exploring the transition states that govern temperature-dependent mechanisms and rates. Kinetic Monte Carlo approaches must be generalized to allow the discovery of new mechanisms, as opposed to reliance upon a priori assumptions of mechanisms. Highly accurate quantum mechanical techniques must be scaled to the appropriate system to determine local minima in energy landscapes and the transformation barriers that exponentially control reaction rates (Figure 20).

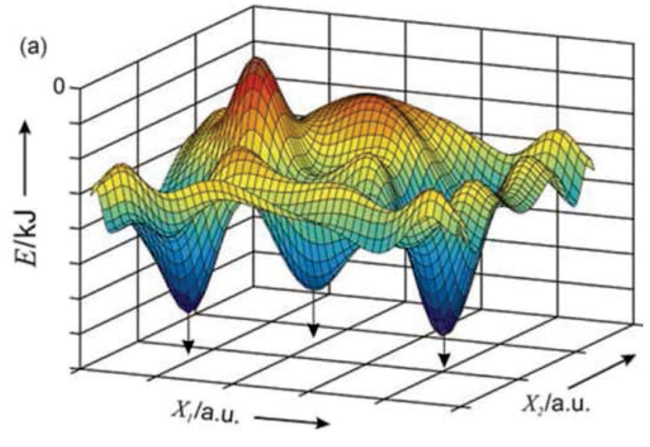


Figure 20. Schematic complex energy landscape highlighting local minima and barriers between them. | Reprinted from J. C. Schön. 2006. Wanderungen in der energie-landschaft, *Physik Journal* 9, 20–22, Wiley permission granted

Potential Impacts

The extreme energy densities associated with nuclear fission reactions, along with the significant impacts on society associated with uncontrolled releases of radiation, necessitate a truly robust understanding of the material and chemical processes that underlie future nuclear energy systems. Understanding the roles of controlling rare events or stochastic processes will facilitate a validated, predictive understanding of materials and chemical responses in these harsh and reactive environments and the extrapolation of laboratory results to conditions outside of the specific conditions (e.g., longer length and time scales). This will lead to the ability to improve descriptions of material behaviors under real-world conditions and of their relationships to potential failures. Ultimately, this perspective will enable the rapid development and deployment of new, long-lived, radiation-tolerant, environmentally resistant materials with enhanced safety, efficiency, and lifetimes. This understanding will be enabled by compositional and microstructural design that is informed by the rare events that affect the long-time behavior of materials and control their lifetimes. It is also expected that such a deep understanding of the material response will lead to the development of non-perturbing sensing capabilities that can be used for detecting deleterious rare events, and perhaps even their precursors, so that the impacts of these events can be mitigated in real time.

3. PANEL REPORTS

As part of the Future Nuclear Energy workshop, panelists were divided into four technical panels to discuss the current status and recent advances in each topic and then outline scientific challenges and opportunities. Their deliberations are captured in panel reports, which are presented in this section of the workshop report. The following are summaries of the panel reports.

The panel on **Design and Discovery of Coolants and Liquid Fuels** addressed the need to understand and design around the numerous, and in some cases conflicting, requirements of the physical, chemical, and radiochemical properties of molten salts for deployment as the coolant or fuel in a reactor. At any instant, the fluid may be heterogeneous and exist in localized equilibria that evolve in time as a result of dynamic chemical and nuclear processes. For example, complex speciation imparted by fission products and trace impurities (including corrosion products) has an unknown effect upon important properties, including heat and mass transfer, which in turn perturb the net thermodynamics, kinetics, and transport in both a chemical and physical context. Understanding these will lead to the development of new molten salt compositions with superior properties which will directly impact the efficiency, safety, and operational lifetimes of next-generation nuclear reactors.

The panel on **Physics and Chemistry of Interfaces** discussed research needs required for understanding the wide range of physical and chemical processes that occur at interfaces, both surface (solid/fluid) and buried (solid/solid), that are proposed for the variety of advanced reactor concepts. These interfaces will have critical impacts on the performance, safety margins, and operational lifetimes of future reactors. To predict and control materials evolution and degradation, this panel concluded that a fundamental understanding of the reaction mechanisms active at the surfaces of and within materials in a complex combination of environments is critically needed. For example, one area identified was the interest in understanding how radiolytic energy, charge, and heat are transported at a variety of solid/liquid and solid/solid interfaces. The impact of defects on the reactivity at interfaces was also viewed as an important issue. Once the fundamental mechanisms of the myriad chemical and physical processes that occur at interfaces are illuminated, this knowledge can catalyze the development of a new generation of materials and coatings designed to control and even repair interfaces exposed to extreme environments.

The panel on **Understanding Behavior at Coupled Extremes** focused on understanding the dynamic and highly coupled processes that occur under extreme conditions. Simple studies of materials and systems at a single given extreme condition were not deemed to be sufficient for these challenges, because of the combination of radiation fields, high temperature, pressure, and stress. These extreme conditions can be synergistic and yield processes and mechanisms that are active only when they are studied concurrently. Only investigations under coupled conditions can provide insight into the full complexity of interfacial reactions, transport phenomena, microstructural evolution, and material defect formation and propagation. As these inextricably linked processes are unraveled, it will be possible to develop new materials, interfaces, and multicomponent systems that survive in harsh, nonequilibrium environments where high-energy, transient species are present.

Discussions in the **Design and Discovery of Structural Materials and Solid Fuels** panel summarized a need for greater fundamental knowledge of nuclear material behaviors based on a mechanistic understanding of the interplay of compositional modifications, defect formation, deformation, and dynamically changing microstructure and nanostructure/chemistry as they are exacerbated by extreme environments. This information will be critical for the development of materials with stable structures at the nano/micro scales that can withstand harsh environments, and even of revolutionary materials that can self-repair. This panel noted that development of robust materials design rules must incorporate holistic understanding of materials and fuels behavior in nuclear energy environments to enable the specification of robust materials and fuels for radiation environments in a way that substantially shortens the current decades-long development cycle.

A major challenge that emerged in the workshop is addressing the multitude of chemical and physical processes that occur in structural materials, coolants, and fuels which must be understood across broad spatial and temporal scales—from atomic to macroscopic length scales and from femtoseconds to years. It was concluded that these requirements, which were common to all four panels, cannot be met with today's analytical and computational tools. Therefore, the **Crosscutting Themes** panel focused on two areas. The first was the need for new characterization approaches that take advantage of in situ measurements, including multiple simultaneous measurements that can probe both chemical reactions and structural changes, to provide a more complete view of the multitude of impacts that occur in the extreme conditions to which these materials are exposed. The second was the development of multiscale modeling capabilities to understand and predict the full range of chemical and physical phenomena that occur under extreme environments. Importantly, it was underscored that experimental methods need to be closely integrated with computational tools to predict and simulate degradation processes, and that deep data analysis will be needed to interpret and assimilate data from multiple experiments. With these approaches, the goal of understanding and predicting chemical and physical changes in materials, coolants, and fuels can be achieved, and will expedite the development of future nuclear energy systems.

Panel A: Design and Discovery of Coolants and Liquid Fuels

Nuclear energy currently provides about 20% of US electricity and approximately 60% of its zero-carbon electricity. In the future, nuclear energy can play a significant role in meeting mid-century energy demands in an environmentally friendly manner; but advanced technologies are needed to replace the current fleet of aging nuclear reactors and move past the limitations of light water reactor technologies. Advanced reactor concepts offer the potential benefits of enhanced safety and reliability, greater resource utilization, improved proliferation resistance, co-production of process heat for industrial operations, and economic competitiveness. In 2002, the Generation IV International Forum (GIF) created a Technology Roadmap that defined the necessary research and development to allow for the deployment of next-generation energy systems after 2030. The GIF selected 6 reactor systems from more than 100 concepts, which were confirmed in the 2014 *Technology Roadmap Update for Generation IV Nuclear Energy Systems*. [OECD 2014] They were the gas-cooled fast reactor, lead-cooled fast reactor, MSR, sodium-cooled fast reactor, supercritical–water-cooled reactor, and very-high-temperature reactor (VHTR). As discussed in the factual status document for this workshop, each reactor technology has its own set of advantages, challenges, and fuel and coolant requirements. To meet the DOE–NE goal “that by the early 2030s, at least two non-light water advanced reactor concepts will have reached technical maturity, demonstrated safety and economic benefits, and completed licensing reviews sufficient to allow construction to go forward,” [DOE 2017] significant research and development is needed to overcome the research challenges and determine the most promising reactor technology.

Recently, there has been growing national and international interest in MSRs because of the potential benefits in higher efficiencies and resource utilization, enhanced safety, and economics. [WNA 2017] In response to this interest, DOE–NE organized a Molten Salt Chemistry Workshop in April 2017 to identify science-based, technology-driven approaches to accelerate MSR development and deployment. [ORNL 2017] High-temperature molten fluoride and chloride salts have many advantages.

1. They can serve as coolants with solid fuels and/or have the fissile or fertile fuel dissolved in the liquid salt.
2. They have excellent heat transfer properties and a high operating temperature that allow for compact design and high operating efficiencies.
3. They are safer (i.e., operate at atmospheric pressure, have a large negative temperature coefficient of reactivity [i.e., when the fuel heats up, it expands and becomes less reactive], and do not react with water or air).
4. The fuel is highly soluble in the coolant.
5. They can be considered for other applications (e.g., solar thermal and metal extraction).

An MSR has the flexibility to operate with a variety of fissile materials, including ^{235}U, ^{233}U, and ^{239}Pu, and can either burn actinides from spent nuclear fuel or use fertile material to generate (breed) fissile material, e.g., ^{233}U from ^{232}Th. However, there are many unique technical challenges that must be addressed because of the chemical nature of the MSR. The chemistry manifested during reactor operation evolves over time because of the generation and decay of fission products and is complicated by the ubiquitous problem of corrosion and reactivity of trace impurities, such as water and oxygen. Reducing conditions and nonaqueous media force the presence of lower-valent actinides, e.g., trivalent and divalent oxidation states; and, depending on the fuel cycle deployed, actinide chemistry from thorium to californium is relevant in these reactors. The increased presence of noble metals and radiation could also result in unexpected reactions during reactor operation. These factors are all compounded by the limited characterization data on the chemical species in a MSR and their impact on the chemical and physical properties. The limited number of studies of complex molten salts means limited data are available on predicting and controlling their behavior. Although there are significant chemical challenges facing the application of molten salts as coolants and liquid fuels in advanced reactors, scientific advancement in these areas offers the greatest opportunities for future reactor concepts and thus was the focus of this panel.

High-temperature, liquid-fueled MSRs have been investigated since 1948, initially as part of a program to develop a high-energy-density nuclear reactor to power an airplane. In 1954, scientists at Oak Ridge National Laboratory (ORNL) demonstrated the concept of a high-temperature fluoride salt–fueled reactor in the Aircraft Reactor Experiment (ARE). The reactor was 2.5 MW(t), fueled with UF_4 (6 mol %) dissolved in NaF-ZrF_4 (53–41 mol %) and moderated with BeO. The reactor operated for 9 days with an outlet temperature of 860°C and was found to be stable and self-regulating. At the end of this program in the late 1950s, MSR technology research was focused on developing a thermal breeder reactor based on the thorium fuel cycle (i.e., ^{232}Th to ^{233}U). From 1965 to 1969, ORNL operated the 8 MW(t) MSRE, which demonstrated many of the key features of a liquid salt–fueled reactor. The fuel for the reactor was initially UF_4 (0.9 mol %, composed of 33% ^{235}U and 67% ^{238}U) dissolved in ^{7}LiF-BeF_2-ZrF_4 (65-29.1-5 mol %), but in subsequent experiments, it was changed to ^{233}U. The salt flowed through a graphite moderator at atmospheric pressure at 650°C. Lithium-7 was used to prevent unwanted formation of tritium from ^{6}Li by neutron-induced fission. The secondary coolant salt was ^{7}LiF-BeF_2 (2:1, FLiBe).

This research showed that the MSR concept was feasible but also highlighted the challenges with salt chemistry, fission product chemistry, analytical chemistry, materials and corrosion chemistry, radiation chemistry, and separations chemistry. [Grimes 1970; Rosenthal et al. 1970] From 1970 through 1976, research at ORNL focused on designing the molten salt breeder reactor, which would use LiF-BeF_2-ThF_4-UF_4 (71.7-16-12-0.3) as the fuel and operate at approximately 700°C. The reactor was to be moderated by graphite, with a 4 year replacement schedule, and the secondary coolant was NaF-$NaBF_4$. Although the MSR program was closed in 1976 in favor of other reactor technologies, this research laid the foundation for a new direction in MSR research. MSRs are now envisioned as a potential way to manage the fuel cycle without aqueous reprocessing of spent fuel and solid fuel fabrication from recycled actinides, provide novel fueling and refueling schemes, and offer a pathway to safer, economical nuclear electricity generation and the co-production of high-temperature, low-pressure process heat for industrial operations. This vision was also recognized by the GIF and has generated significant national and international interest in MSR research. [WNA 2017]

Current Status and Recent Advances

Currently, a wide variety of MSR concepts are being considered using fluoride or chloride salts. [ORNL 2017] MSRs under consideration today are either solid-fueled salt-cooled or liquid salt–fueled designs. In solid-fueled salt-cooled reactors, such as the VHTR or Advanced High Temperature Reactor (AHTR) (also known as the fluoride salt–cooled high-temperature reactor), the molten salt (i.e., the primary fluid) flows over a solid ceramic fuel in the form of prisms, plates, or pebbles. A secondary fluid, which can also be a molten salt, removes the heat from the primary fluid in a heat exchanger to generate power via gas or steam turbine. Molten salts have excellent heat transfer properties, similar to those of water, and have the advantage of operating at low (atmospheric) pressure. In liquid salt–fueled reactors—such as the ARE and MSRE—the fissile or fertile material and the fission products are dissolved in the molten salt that circulates through the primary heat exchanger. Heat is removed by a secondary (molten salt) coolant to generate electricity. The reactor can operate as a burner or converter (i.e., consuming more fissile material than it makes) or a breeder, which makes more fissile material than it consumes (e.g., ^{233}U from ^{232}Th).

The choice of molten salts depends on whether the salts are used as the solvent for the fissile or fertile fuel, as the primary coolant (as in the AHTR), or as the secondary (heat transfer) coolant. As discussed by Grimes [1970] for the MSRE, for applications as the fuel or primary coolant, the elements must have a low neutron capture cross section and good moderating properties at the neutron energies of the reactor (i.e., fast or thermal) (Figure 21). The salt must dissolve more than a critical concentration of fissile material (^{235}U, ^{233}U or ^{239}Pu) and must dissolve the fission products without loss of physical properties (Figure 22). One of the challenges is to determine which fission products remain dissolved in the salt, which are volatile, and which ones precipitate on surfaces (and where). The salt must be stable against radiation and high temperatures, and it must possess low vapor pressure over a wide operating range (500–750°C for MSR and up to 900°C for AHTR). The salt must possess good heat transfer and hydrodynamic properties to serve as a heat transfer fluid. [Williams et al. 2006] It also must be compatible with the reactor and moderator materials.

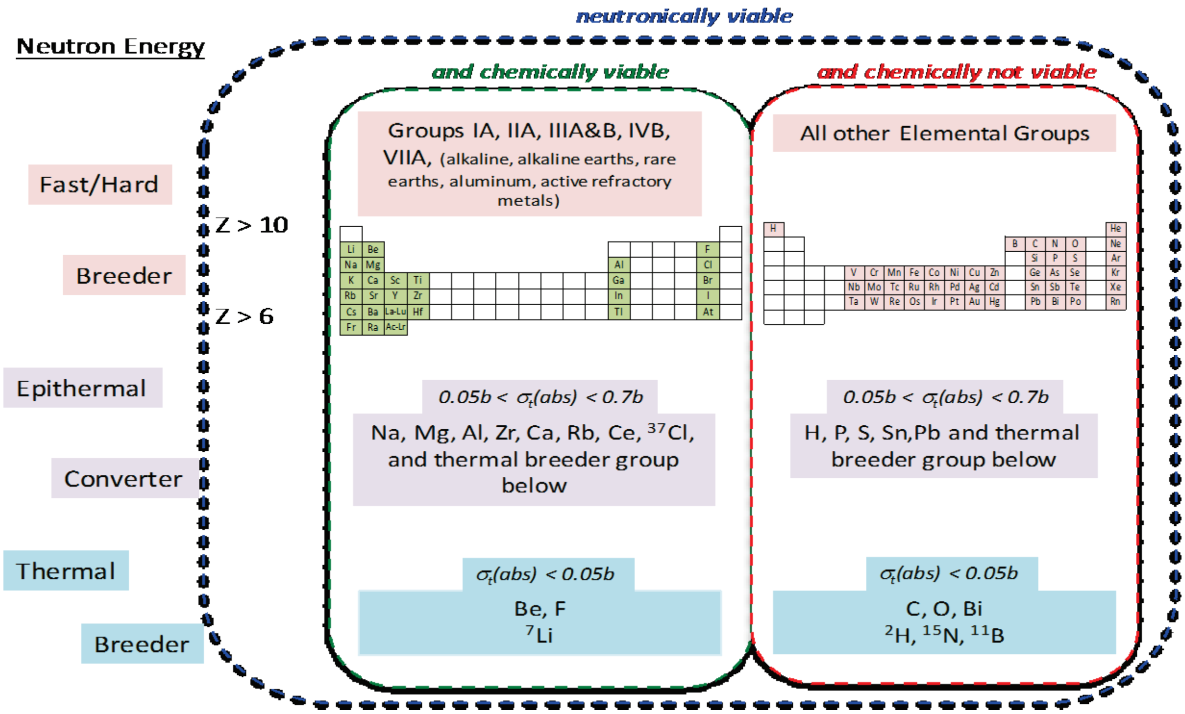


Figure 21. Approach to screening candidate molten salts for the MSRE (where σ_t(abs) is total neutron absorption cross-section). | Image courtesy of Oak Ridge National Laboratory

Finally, the salt should be low in cost, be economical to purify, and allow separation of fission products and recovery of bred and unburned fissile materials. Examples of fluoride fuel salts primarily for thermal spectrum applications include (1) ^{7}LiF and/or NaF and BeF_2 combined with low concentrations (<5 mol %) of UF_4/PuF_3 and (2) ^{7}LiF and/or NaF and high concentrations of UF_4/ThF_4 (near eutectic: 25–30 mol % actinide). For fast neutron energies, chloride salts have some attractive features compared with the fluoride salts; specifically, the chloride salts have higher solubility for the actinides, and the actinide trichlorides form lower melting solutions. However, because of the high melting point of NaCl, other salts need to be mixed in, such as $MgCl_2$, KCl, or LiCl, to lower the melting point. Also, Na^{37}Cl is preferred because ^{35}Cl produces ^{36}Cl, a long-lived energetic beta emitter, as an activation product.

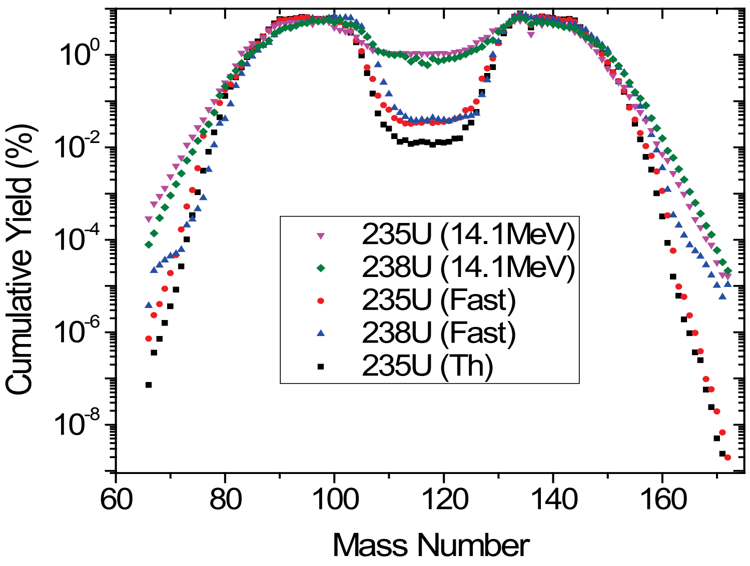
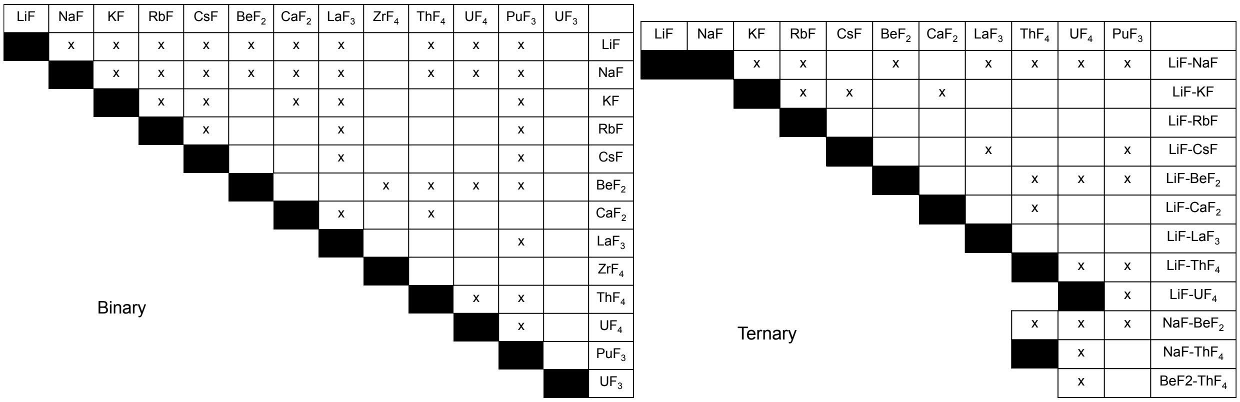


Figure 22. Fission products (atomic mass on the x-axis) arising from various neutron environments. Note the increased production of noble metals in the presence of a fast (2 MeV) spectrum relevant to certain molten salt reactor designs. | Image courtesy of Michael A. Koehl, Colorado School of Mines

The secondary coolant does not need to meet the neutronics and radiation resistance requirements of the primary coolant. However, it does have the same heat transfer, hydrodynamic, and materials compatibility requirements. These properties include melting point, vapor pressure, viscosity, density, heat capacity and volumetric heat capacity, and thermal conductivity. The salt also should be chemically stable and not react with water or air in the event a leak develops. Numerous reports have reviewed and summarized the literature for molten salt coolants as the primary coolant [Williams et al. 2006; Samuel 2009; IEA 2013] or secondary coolants. [Williams 2006] These reports have also highlighted the gaps in the thermodynamic data for candidate molten fluoride salts and the even greater lack of data available for chloride salts (Figure 23).



Binary

LiF	NaF	KF	RbF	CsF	BeF_2	CaF_2	LaF_3	ZrF_4	ThF_4	UF_4	PuF_3	UF_3	
■	x	x	x	x	x	x	x		x	x	x		LiF
	■	x	x	x	x	x	x		x	x	x		NaF
		■	x	x		x	x				x		KF
			■	x			x				x		RbF
				■			x				x		CsF
					■			x	x	x	x		BeF_2
						■	x		x				CaF_2
							■				x		LaF_3
								■					ZrF_4
									■	x	x		ThF_4
										■	x		UF_4
											■		PuF_3
												■	UF_3

Ternary

LiF	NaF	KF	RbF	CsF	BeF_2	CaF_2	LaF_3	ThF_4	UF_4	PuF_3	
■	■	x	x		x		x	x	x	x	LiF-NaF
		■	x	x		x					LiF-KF
			■								LiF-RbF
				■			x			x	LiF-CsF
					■			x	x	x	LiF-BeF_2
						■		x			LiF-CaF_2
							■				LiF-LaF_3
								■	x	x	LiF-ThF_4
									■	x	LiF-UF_4
								x	x	x	NaF-BeF_2
								■	x		NaF-ThF_4
									x		BeF2-ThF_4

Figure 23. Available thermodynamic data (marked by "x") for binary and ternary fluoride salt mixtures for MSRs, developed at the Institute for Transuranium Elements of the Joint Research Centre of the European Commission, Karlsruhe, Germany. | Reprroduced from E. Capelli, *Thermodynamic Characterization of Salt Components for Molten Salt Reactor Fuel*, Figure 1.2, PhD Thesis, University of Delft, 2016.

To optimize a molten salt for a particular application, many criteria must be met and many experimental parameters measured. In most cases, mixtures of salts are used to obtain the desired properties because the melting point of an individual salt is too high for coolant applications (e.g., the melting point of LiF is 845°C). Since each salt mixture and salt composition will have different physical and chemical properties, and these properties will impact the solubility of fission products and impurities, the amount of experimental data that is needed to discover or optimize a molten salt mixture is extremely large. Phase diagrams are the most important tool for understanding fuel and coolant salt properties; but other physical properties need to be measured for individual salts and mixtures—including vapor pressure, viscosity, density, heat capacity and volumetric heat capacity, and thermal conductivity, and surface tension. Many of these properties are sensitive to impurities, including dissolved metals and oxygen-containing impurities such as oxides, hydroxides, sulfates, carbonates, and oxyhalides. Therefore, rigorous methods must be developed to prepare high-purity samples, and rigorous analytical practices are needed to make reproducible measurements. Given the number of measurements required and the large variety of experimental variables, high-throughput methods need to be developed to accelerate precise property measurement and database generation. Computational methods and thermodynamic models are also needed to rapidly advance the exploration of molten salt properties to enable materials-by-design approaches.

Since the original ARE and MSRE, there have been many advances in experimental, computational, and analytical methods to explore the structures, properties, and reactivities of molten salts. Since thermodynamic properties are determined by atomic structure and inter-atomic interactions, modern spectroscopy methods can provide new insights into the structure and dynamics of molten salts. For example, modern x-ray and neutron scattering—along with optical spectroscopy, nuclear magnetic resonance (NMR), and spectroelectrochemistry methods—can provide quantitative insights into the oxidation states of transition metals, lanthanides, and actinides, and the local structure and bonding. [ORNL 2017] One of the challenges is providing sample environments in which these measurements can be made at high temperatures (up to 1000°C) in the presence of radioactive species (although surrogates can be used for many studies). These data can then be used to validate computational calculations to predict thermodynamic properties, especially for difficult-to-measure sample environments (i.e., high temperature and high radiation).

The development of computational methods to predict optimal molten salt compositions, properties, and reactivities would dramatically increase the rate of scientific discovery. However, a multiscale approach must be employed, and there are serious computational challenges associated with these types of computational methods. At the molecular level, static ab initio methods must be able to accurately account for relativistic effects and determine properties like oxidation and reduction potentials with a high level of fidelity. Time-dependent chemical reactions necessitate ab initio molecular dynamics, for which increased compositional complexity mandates the inclusion of extended polarization effects and longer simulation time scales that can probe the role of fluctuations in external conditions. [Bengtson et al. 2014; Song et al. 2017] At longer length and time scales, classical molecular dynamics (MD) simulations are needed to predict the physical and transport properties of molten salts, and they can be applied to understanding interfacial behavior that can lead to materials degradation. Such approaches will require benchmarked numerical descriptions of the interatomic interactions (force fields). Ultimately, to achieve predictive insight across scales—from the atomic and molecular chemical reactivity to bulk thermophysical and transport properties—a combination of quantum mechanics, classical dynamics, course-gained models, continuum models, and thermodynamics models must be integrated. Doing so will require the use of DOE's high-performance computing resources.

Scientific Challenges and Opportunities

To push forward the development of advanced reactor concepts and realize the potential benefits of enhanced safety, reliability, resource utilization, and proliferation resistance, many fundamental challenges need to be overcome. The application of molten salts as coolants and liquid fuels in advanced reactors offer the greatest opportunities for future advanced reactor concepts, but there are significant chemical and materials challenges that need to be addressed. The scientific challenges and opportunities for molten salts are organized into three key areas: (1) time-dependent radiochemical processes, (2) trace constituents in extreme environments, and (3) tailored interfaces for extreme environments, which are discussed in detail in the following sections.

Time-dependent radiochemical processes

One of the challenges in a liquid salt–fueled reactor is time-dependent radiochemical processes. Understanding the fate and transport of fission products is key to controlling the salt chemistry/properties and reactor performance. Although the decay pathways of fission products are well understood and independent of the chemical environment (see Figure 22), the chemical and physical properties of these elements and their interactions with the environment are different at each step of the decay chain. A key challenge is to understand the solubility of the fission products as a function of system composition (chemical potentials) and external variables. [Compere et al. 1975] In early studies of the MSR, noble gas behavior was of particular interest because those gases are neutron poisons, i.e., neutron absorbers, that can affect the performance of the reactor. For example, ^{137}I ($t_{1/2}$ = 24 s) is soluble in the fluoride molten salt but decays to become an entrained noble gas, ^{137}Xe ($t_{1/2}$ = 3.8 min), which will further decay to ^{137}Cs ($t_{1/2}$ = 30 years). If the gas is removed from the salt, radioactive cesium will plate in the outgas system; but if the xenon gas stays entrained in the salt, the resulting cesium will be soluble, based on its free energy as the fluoride salt. Thus, there is a need to understand the binding, coordination environment, and Lewis acid-base properties of the fission products. Although individual elements can be experimentally studied with (nonradioactive) surrogates, it is difficult to study the dynamics and changing chemistries of short-lived fission products. Thus, computational methods are needed to complement experimental studies to understand the chemical and physical properties of short- and long-lived fission products.

Another key challenge is to understand how the fission products change the chemical and physical properties of the salt mixtures as a function of time. For example, the redox potential of the melt may change with fission; and free halide ions could be released, which change the Lewis acid-base properties of the melt and the corrosivity (i.e., fission of $^{235}UF_4$ can produce $^{141}Ba^{2+}$ and ^{92}Kr and free fluoride ions). Understanding how fission products interact with the reactor materials is also important. In the MSRE, it was found that the fission product tellurium contributed to surface cracking of the walls of the reactor by leaching chromium from the Hastelloy N alloy. [Keiser 1977] Understanding whether the fission products change thermophysical properties of the salt—such as thermal conductivity, melting point, viscosity, and heat capacity—is also important for efficient reactor operation.

Fission liberates large amounts of energy, as both electromagnetic radiation and kinetic energy of the fragments, into the local environment. This process is repeated with many various outcomes for each fission product, and the impacts on the physical and chemical properties of the molten salts need to be understood. During the MSRE project, the fluoride fuel and coolant salts appeared to be relatively immune to irradiation damage, and any primary radiolytic event was rapidly reversed by recombination. However, the long-term (>5 years) impact of high radiation fields on a molten salt is not known. If the fluoride molten salt was allowed to solidify and cool below 200°C, significant radiolysis and chemical changes occurred. [Williams et al. 1996] Chloride salts have not been studied under the high radiation fields found in MSRs. However, molten alkali chloride salts have shown good chemical and radiation stability in pyroprocessing of spent nuclear fuel. Nevertheless, experiments need to be conducted with chloride salts under more intense irradiation conditions, as would be found in a MSR, to confirm their stability and identify any reaction products.

To study the time-dependent processes relevant to an MSR, real time in situ characterization tools are needed that operate in extreme environments (high temperatures and radiation fields) to monitor the species in solution. Optical (ultraviolet-visible-infrared and Raman) spectroscopy, electrochemical, and spectroelectochemical methods in conjunction with chemometric methods can be used to provide quantitative information on the identity, concentration, and oxidation states of dissolved species in complex, multicomponent solution. To determine the structure and bonding of species in molten salts, neutron diffraction and x-ray absorption spectroscopy can be applied at high temperatures. High-temperature solid state and liquid NMR can also provide insights into the local structures of species in molten salts, since many of the species are NMR-active, including $^{7}Li^{+}$, $^{19}F^{-}$, $^{23}Na^{+}$, and selected lanthanide and actinides (including $^{235}U^{3+,4+}$) cations.

Computational methods are needed to predict the solubility of fission products, the impact on thermophysical properties, and the fate and transport of fission products, especially for short-lived species and those that are hard to measure experimentally. There is also a need to fill data gaps for the properties of the molten salts by using modeling and simulation. Computational predictions for molten salts are a major scientific challenge because of the complex nature of the salts and the molecular, mesoscale, and macroscale processes that occur over a wide range of time scales (from nanoseconds to years). As a start, experimentally validated predictive computational methods that employ first-principles molecular dynamic simulations are needed to describe the structure and dynamics of molten salt systems. Understanding and predictions of the compositional and redox changes that arise as a result of fission, as well as the solubility and transport of the fission products, are needed. Understanding the fates of insoluble fission products (i.e., where they deposit and why) is important for safe operation of the reactor. Ultimately, quantum mechanics, classical dynamics, coarse-grained models, continuum models, and thermodynamic models need to be integrated and validated with experimental data to enable predictive insights on chemical reactivity at the atomic level to thermophysical and transport properties. Computational studies will require large-scale simulations with tens of millions of atoms to cover the spatial scale and will require the use of DOE's high-performance computers with optimized exascale software codes.

Addressing the scientific challenges described will have significant scientific impacts on advanced nuclear reactors, as well as other areas of energy technology. Characterization and computational tools will be available for time-dependent phenomena to monitor the health of systems in real time and enable predictive system response to perturbations. These tools could be used in other areas beyond MSRs, including catalysis, batteries, corrosion, and pyroprocessing. New insights will also be gained into complex chemistry in extreme environments (i.e., high temperature and high radiation fields). These studies will also enable improved heat transfer, a better understanding of actinide chemistry, and insights into processing of molten salt fuels and coolants.

Trace constituents in extreme environments

One of the challenges in molten salt chemistry is understanding the evolution and reaction chemistry of the trace constituents (ppm or less) and their impact on the thermophysical properties of a molten salt mixture. Trace constituents include impurities, activation products such as tritium, corrosion products, and low concentrations of fission products. New characterization techniques need to be developed to quantitatively determine the concentration levels of constituents at low concentrations (ppm or less), as well as follow their reactions in real time under extreme environments. As discussed earlier, optical spectroscopy and electrochemical methods coupled to chemometrics hold great promise, but the levels of detection need to be pushed below ppm levels. New approaches to low-level detection of elements in a complex matrix could exploit the resolving power and large dynamic range of mass spectrometry. However, a sampling method is needed for real-time analysis of molten salts at high temperatures. These analytical tools could then be coupled to high-throughput methods to collect data on the large number of species present under a variety of experimental conditions while measuring the properties of the solutions. A major advance would be to extend these studies to include radiation fields and radioactive materials, since there are a limited number of experimental facilities that can perform these kinds of experiments. High-throughout methods would greatly accelerate the generation of databases of a variety of thermodynamic properties of molten salts and accelerate the discovery of new molten salts with superior stability, low reactivity, and excellent heat transfer properties.

Corrosion can result from reactions of trace impurities or fission products with the reactor materials. [Delpech et al. 2010] For example, corrosion rates for salts that were used as received and remained open to the atmosphere were four orders of magnitude higher than those obtained for purified salts in a closed loop. [Mishra and Olson 2005] Oxidizing impurities typically found in molten salts include water and hydrogen fluoride, but they may also include metallic impurities. Other corrosive impurities that must be removed include oxides, hydroxides, sulfates, sulfides, and carbonates. In molten salts, corrosion depends directly on the thermodynamic driving force of the corrosion reactions, since the products of metal corrosion by fluoride melts are soluble (e.g., $Cr + 2HF \rightarrow CrF_2 + H_2$) in the molten salt and passivation is precluded. [Grimes 1970] Thus, thermodynamic data are needed for the metals, trace constituents, and potential halide-containing reaction products to determine if a reaction will occur over the operating temperature range. This information will facilitate the design of chemically stable reactor materials.

The ability to use computational methods to understand the impacts of trace constituents on the chemical and physical properties of molten salts will be valuable in accelerating the development of stable reactor materials and improving the operational efficiency and lifetimes of reactors. Static and dynamic ab initio methods are needed to model redox states and chemical reactions in solution, and classical MD simulations are needed to model transport properties. One goal is to develop computational methods that can predict the properties of systems with ppm levels of impurities and obtain accurate results. Computational methods can also be used to extrapolate limited experimental data into extreme environments of high temperature or high radiation fields.

Addressing these scientific challenges will have significant scientific impacts. These advances will lead to an improved understanding of how trace constituents impact chemical properties and system efficiencies in MSRs and other systems. They will enable improved understanding of other complex electrolyte systems and develop new computational and experimental techniques. These studies will lead to an improved understanding of fundamental structure, binding, and reactivity of actinides; and the advances in characterization tools will lead to improved methods to deal with low-level impurities in a variety of energy applications. Overall, these advances will lead to an improved understanding of the roles of trace elements in corrosion and in improved reactor performance and longer reactor lifetimes.

Tailored interfaces for extreme environments

Materials compatibility of molten salts under extreme environments has been a key challenge ever since the ARE and MSRE and a potential bottleneck to their future use as coolants and fuels. There is a need to understand, at the molecular level, the structure and chemical reactivity at the fluid/solid interface to provide important insights into corrosion by fission products and their adsorption onto surfaces—such as metal alloys and graphite—and to aid in the design of new materials with interfaces tailored for improved material lifetimes and performance under extreme environments. There are still unresolved questions about chemical compatibility and embrittlement by fission products, and some recent MSR designs are proposed to operate at higher temperatures and use chloride salts. [WNA 2017; ORNL 2017] Much less is known about the compatibility of chloride salts with structural materials for MSR applications, and some studies appear to show greater corrosion resulting from chloride than from fluoride salts. In addition to the effects of corrosion, radioactive fission products may deposit at interfaces, providing a fixed source of radiation and heat. Their presence would impact reactor operation and maintenance, and deposition of neutron poisons on the (graphite) moderator in the core would impact reactor performance (see Table 1).

Table 1. Fission product distribution in the fuel, on the graphite moderator, on the Hastelloy reactor walls, and in the purge gas of the MSRE. | *Source:* W. R. Grimes. 1970. Molten-salt reactor chemistry, *Nucl. Appl. Technol.* 8(2), 137–155.

Nuclide	**Quantity found (% of calculated inventory)**				
	In fuel	**On graphite**[a]	**On Hastelloy-N**[a]	**In purge gas**[b]	**Total**
^{99}Mo	0.17	9.0	19	50	78
^{132}Te	0.47	5.1	9.5	74	89
^{129}Te	0.40	5.6	11.5	31	48
^{103}Ru	0.033	3.5	2.5	49	55
^{106}Ru	0.10	4.3	3.2	130	138
^{95}Nb	0.001 to 2.2	41	12	11	61
^{95}Zr	94	0.14	0.06	0.43	95
^{89}Sr	83	8.5	0.08	17	109
^{140}Ba	96	1.9	0.05	0.48	98
^{141}Ce		0.33	0.03	0.88	
^{144}Ce		0.92	0.03	2.7	
^{131}I	60	0.11	0.3	19	80

[a] Calculated on assumption that average values for surveillance specimens are representative of all graphite and metal surface in MSRE.
[b] These values are the percentage of production lost assuming mean values found in gas samples apply to the 4-liter/min purge.

To investigate the reaction, transport, and deposition of fission products at the fluid/solid interface will require the development of characterization methods and sample environments to study surface reactions in situ under extreme environments. Computational methods need to be combined with experimental data to help describe the reactions at the interface and gain predictive insights into designing stable fluid/solid interfaces over a wide range of time scales. Methods also need to be developed to aid in the design of new materials, with knowledge of the molten salt and fission product chemistry and radiation effects so interfaces can be tailored to resist corrosion and keep their structural integrity.

Most corrosion studies to date with molten salts have relied on macroscopic ex situ measurements under static conditions and postmortem analysis, typically by transmission electron microscopy with energy-dispersive spectroscopy. This approach leaves a gap in the understanding of the molecular structure, species, and dynamics at the liquid/solid interface and the kinetic parameters that determine their evolution. For example, studies of the compatibility of the $NaBF_4$/NaF coolant with Hastelloy N (in a convection loop) found the loop partially plugged after 8765 h of operation at 607°C. Postmortem analysis found deposition of Na_3CrF_6; and large quantities of Cr, Fe, Ni and Mo—which are major elements in Hastelloy N—were found in the salt. [McCoy et al. 1970] New in situ characterization methods and sample environments are needed for extreme environments to characterize the molecular-level chemistry in real time to understand interfacial reactions in molten salts, including redox reactions, precipitation, and diffusion of fission products into metal (or graphite) or leaching of metal into solution. A number of surface-sensitive optical spectroscopy techniques (e.g., reflection-adsorption infrared spectroscopy, sum frequency generation, and surface-enhanced Raman) and x-ray and neutron scattering techniques (e.g., reflectometry and grazing incidence angle), in combination with electrochemical methods can be used to probe the reactions, the metal species, and the oxidation state of the salt phase at the interface. To aid in the understanding of interfacial reactions under more realistic conditions, experiments should be run under flowing salts, in a flow loop, to capture the impact of thermal gradients, fretting, and erosion on the mechanistic studies. The combined effects of chemistry and radiation on corrosion should also be studied because of the potential for synergist effects. Characterization of deposits that form at the interface, as well as of any elements leached from the surface, will provide a greater understanding of the chemical reactions and the reaction kinetics among the molten salt, fission products, and reactor material. Understanding the interfacial chemistry in situ and under realistic condition will help in predicting materials behaviors and lifetimes and accelerate the development and deployment of new materials suitable for MSRs and for other applications under extreme environments.

Another important interface that needs to be controlled is the gas/liquid interface. In the MSRE, the salt mixture was sprayed into the gas space of the pump bowl, above the sump pump, to allow noble gases such as krypton and xenon (a neutron poison)—which are only sparingly soluble in the fluoride salts—to be removed by a helium sweep gas. Tritium, a moderate-lifetime beta emitter, is also produced by both ternary fission and a number of light-element neutron reactions. Because of its high mobility through alloys at high temperatures, it is important to understand its reactions at the gas/solid and gas/liquid interfaces. Tailoring of interfaces to prevent the diffusion of tritium would be a major advance. Another interfacial process that it is important to understand is mist formation in the pump bowl, which can carry nonvolatile fission products into the gas stream (see Table 1). It is critically important to understand the nucleation of particles and transport of fission products across the gas/liquid interface and gas-phase entrainment to account for the radioactive inventory and for the safe operation of the reactor. It is difficult to experimentally study the gas/liquid interface. Therefore, this topic is an ideal challenge for computational modeling, in which first-principles calculations can be combined with classical MD simulation using validated force fields, and with mesoscale simulation, to provide predictive insights into behavior at the gas/liquid interface.

One of the challenges in using molten salts as coolants and fuels is finding a material that is corrosion-resistant, radiation-resistant, and structurally strong. A classic approach to corrosion protection is to apply a coating onto a structural material, but oxide coatings dissolve in molten salts. The free energy driving force for corrosion in molten salts is controlled by the redox potential of the salt matrix. It has been shown that reducing conditions (resulting from varying the U^{3+}/U^{4+} ratio, for example) suppress corrosion; but they have been found to make other reactions between the salt and the solid, such as alloying, more likely. [Williams et al. 2006] Thus, a delicate balance is needed between oxidative and reductive degradation, and real-time monitoring is needed to control the redox properties of the salt. If a coating could be developed that controls the redox potential of the interface relative to the molten salt and fission products, and a method could be found to bond the coating, a corrosion-resistant structural material could be developed. To advance the design of new materials, computational studies are needed to guide the choice of corrosion-resistant materials. Novel processing methods, such as additive manufacturing, are needed to tailor the properties of the interface by adjusting the chemical composition, by causing microstructural morphology of the structural component, or by developing novel methods to bind the coating to the structural material. These approaches could also have the advantage of reducing the time required to qualify a material for an application.

There is a need to develop computational models to describe molecular, mesoscale, and macroscale interfacial processes over a wide range of time scales (from nanoseconds to years) to gain a predictive understanding of interfacial processes and to gain insights into the design of new tailored interfaces. Doing so requires multiscale simulations that couple information from first principles studies to classical MD to mesoscale simulations to address several key challenges—including predicting slow processes, such as corrosion, transport processes at the gas/liquid and liquid/solid interfaces, nucleation and growth of deposits formed at interfaces, and coupling of radiation and chemical reactions. These studies would feed into the development of new alloys and tailored interfaces for extreme environments.

Addressing these scientific challenges will improve the understanding of corrosion mechanisms in alloys and compositionally graded surfaces. This will enable the design of new engineered materials with tailored interfaces for use under extreme environments with predicted lifetimes. Understanding the transport of fission products in the gas phase and at gas/solid and gas/liquid interfaces would also improve the safety and operation of the reactor. New in situ surface-sensitive tools need to be developed to monitor the health of the reactor materials in real time; these could be used for other applications under extreme environments.

Conclusion

Molten salt coolants and fuels offer the potential benefits of enhanced safety, reliability, resource utilization, and proliferation resistance; but there are many fundamental chemical and materials challenges that need to be addressed. Since the original work with the first MSR in the 1960s and 70s, there have been significant advances in analytical tools, especially x-ray and neutron scattering, that can be applied to in situ measurement of the structure and dynamics of molten salts in extreme environments. There also have been advances in computational methods for predictive understanding of the structure, dynamics, reactions, and thermodynamics of molten salts. These tools will help provide a deeper fundamental understanding of chemical and physical properties of molten salt, which will aid in the design of new salt compositions with superior properties. Understanding the solubility, reaction, and transport of fission products and trace constituents in molten salts will aid reactor design, operation, waste management, and safety. New corrosion-resistant materials can be designed from a knowledge of the interfacial reactions of the molten salts, fission products, and trace constituents to improve reactor lifetimes. To realize the potential for molten salts as coolants and fuels, new fundamental understanding is needed of chemical and physical properties of molten salts and their interactions and reactions with fission products, reactor materials, and trace constituents under extreme environments.

Panel B: Physics and Chemistry of Interfaces

Future reactor designs under consideration that employ gas, liquid metal, and molten salt coolants will operate under increased temperatures (600 to 1100°C) along with higher radiation fluxes (order of magnitude increases in the displacement damage). Further, these new reactor designs will need to be operated efficiently and reliably over decades of performance with minimal upkeep. These challenging conditions will require materials for use in those reactors with performance characteristics far beyond those of current materials. In particular, surfaces and interfaces in structural materials and fuels must withstand reactor conditions under irradiation, corrosion, and other types of extreme conditions without increased downtime or operational risk. Much of the damage incurred in these materials occurs at interfaces. Tailoring of surfaces exposed to fluids (gases/liquids) and buried interfaces (solid/solid interfaces) will be essential to the development of material systems to reach the elevated damage, temperature, and corrosive environments that are proposed for next-generation reactors.

A greater understanding of the myriad chemical and physical processes that occur at these various types of interfaces is critically needed to control and even mitigate these processes. Controlling interfaces under reactor operation, used fuel storage and disposition, and accident conditions for reactor operation and used fuel storage will contribute to increased stability and safety margins. Increasing the interfacial performance of materials by enhancing the stability of surfaces for advanced reactor environments (high temperature, radiation, and pressure, among others) will lead to reduced corrosion and erosion of materials and minimize the transport and deposition of radioactivity within future gas, liquid metal, and molten salt reactor concepts. Improvements in fuel behavior in advanced reactors, enabled by increased understanding of the evolution of internal interfaces within fuels and structural materials, will produce fuels and claddings better able to withstand higher burnup, higher temperature gradients, and harsher corrosive environments. Equally, the nature of the coolant and its chemistry at high temperatures under radiolytic conditions is a crucial determinant of interfacial material degradation. Likewise, the development of a capability to predict defect interactions at solid/solid internal interfaces, such as interphase and grain boundaries, precipitates, and dispersoids, will provide the scientific underpinning for the microstructural design of advanced materials with tailored responses in future nuclear technologies.

Current Status and Recent Advances

Solid/fluid interfaces

Radiation-induced processes at and near interfaces contribute to corrosion, dissolution, hydriding, catalysis, and many other phenomena that impact nuclear energy technologies. In fact, radiolysis effects at interfaces may be quite different from those that occur in the bulk material. Further, radiation energy absorbed in one phase may contribute to the chemistry in the other one, significantly increasing the effective yields of the radiolytic products (Figure 24). Interfacial energy transfer involves interactions of active species, charges, and excitations between the contacting phases. For example, radiation-chemical yields of H_2 with respect to the radiation energy deposited to water adsorbed on an oxide surface may increase 10- to 100-fold relative to bulk water [Petrik 2001; Poston 2014]; and on the surfaces of alkali halide salts, they increase 10,000- to 100,000-fold. [Alexandrov 1987]

Detailed mechanisms of such efficient energy transfer are not well understood, but it is believed that low-energy electronic excitations generated in solids (e.g., electrons, holes, excitons, or mobile defects) may play a decisive role. [Petrik 2001; Poston 2014] Typically, mobile excitations generated by radiation in a certain subsurface layer (from nm to µm thick) may reach the interface during their lifetimes and react with the adsorbed coolant molecules. The flux of the excitations to the interface depends on a variety of parameters, including the trapping defect density in the bulk, and can be controlled by doping. For example,

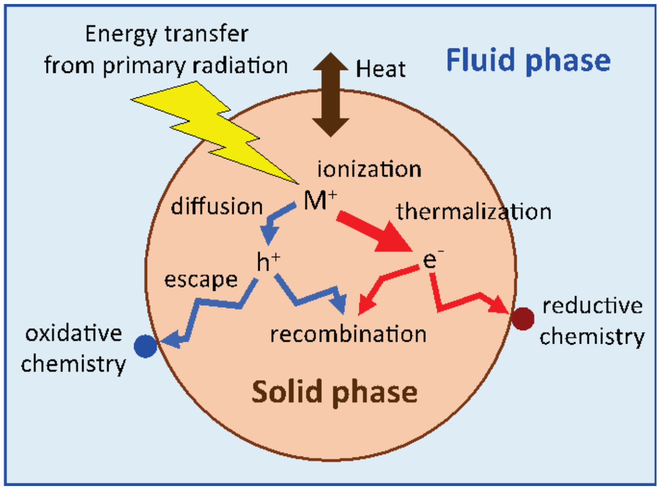


Figure 24. Radiolytic energy delivered near interfaces or into nanoparticles can result in higher yields of charge separation and reaction products in the surrounding fluid phase as a result of migration of radiolytic species to the interfacial region. | Image courtesy of James Wishart, Brookhaven National Laboratory

~0.3% of Nb^{5+} in ZrO_2 completely suppresses energy transfer to adsorbed water and thus H_2 production. [Petrik 2001] Interfacial energy transfer is most efficient for low-dimensional systems—thin films, nanoparticles, and porous materials—in which a larger fraction of the mobile excitations can reach the surface. These excitations can induce chemistry in molecules adsorbed at or near the interface. The various mechanisms are complex and insufficiently understood. They depend on the electronic structures of the adsorbate and the adsorbent at the surface, where non-idealities (such as structural and compositional defects and impurities) could play important roles.

Our understanding of processes at liquid/solid interfaces (e.g., corrosion, oxidation, deposition) is mainly limited to water-based reactor conditions. While this body of knowledge informs our approaches, interfaces with molten salts, liquid metals, and gases under high temperature (and/or pressure) conditions pose many new challenges. Very little is known about the generation, migration, and reactivity of electronic excitations and polarons (holes and electrons) and their subsequent chemical effects near the interfaces of new-generation nuclear materials with reactive media.

Filling this knowledge gap will require the coordination of experimental and theoretical investigations involving multidisciplinary teams of chemists, material scientists, physicists, engineers, and computer scientists. Experimental techniques with ultrafast time resolution and ultrahigh spatial resolution can reveal initial charge and energy transfer events that lead to interface degradation and ultimately corrosion. These include pulsed irradiation (electrons, photons, and ions) in combination with time-resolved detection methods (e.g., optical and vibrational spectroscopy, luminescence, mass spectrometry) to apply reaction dynamics and surface science methods for the mechanistic characterization of interfacial reactivity and its impact on surface transformation (e.g., oxidation, corrosion, new phase formation). New in situ and operando methods for investigating interfacial catalysis have enabled many scientific advances, spurred along by the tremendously increasing performance of synchrotron and neutron facilities, advanced imaging, and other analytical techniques. These methods need to be adapted to the demanding environmental conditions expected in future nuclear technologies.

Computation plays an extremely important role in understanding the chemical and structural evolution of heterogeneous systems, in which continuum models and empirical relations do not apply. A prime example of this is the field of low-temperature molten salts (ionic liquids). True comprehension of the molecular origins of their complex physical behavior on multiple length and time scales has been enabled only by molecular dynamics (MD) simulations of increasing sophistication. [Freitas 2014; Shimizu 2016] Quantum MD simulations can follow the evolution of excess charges produced by radiolysis, which is the first step in understanding the reactivity of ionic liquids. [Xu 2015] Events on the molecular scale impact the reliability of nuclear systems only if their effects cascade to ever-larger dimensions; thus, it is important to connect to simulations on larger scales, up to macroscopic systems, in a multiscale computational framework. MOOSE-BISON-MARMOT is an example of a computational framework that has been developed to model the evolution of nuclear fuel in tight integration with experiment. Similar integration of multiscale computational tools is essential to establish a mechanistic understanding that will permit informed tailoring of materials and interfaces for durable and reliable nuclear systems.

Solid/solid interfaces

Most damage processes in materials initiate at solid/solid interfaces, including the formation of voids and fission gas bubbles, solute and impurity segregation, depletion, clustering, and phase transformation. These atomic-level processes eventually lead to material failure: swelling, hardening, intergranular cracking, fast corrosion along grain boundaries, degradation of thermal conductivity, and other types of deterioration. [Brinkman 1954; Sickafus 2007] The current understanding of these processes is mainly qualitative and limited to observations and phenomenological modeling. Thus, our knowledge of these processes falls far short of providing the scientific underpinning necessary to design materials for the sorts of tailored responses required for the development of future nuclear systems. New understanding of radiation-tolerance mechanisms has recently been gained through the systematic design of materials with tailored interfaces and the integration of experiments with theory and computation [Han 2013; Beyerlein 2013; Demkowicz 2010] (Figure 25). However, insights from altering single-dimensional variables (e.g., grain size, layer thickness, particle size or spacing) are not sufficient for designing materials for radiation tolerance and damage inhibition.

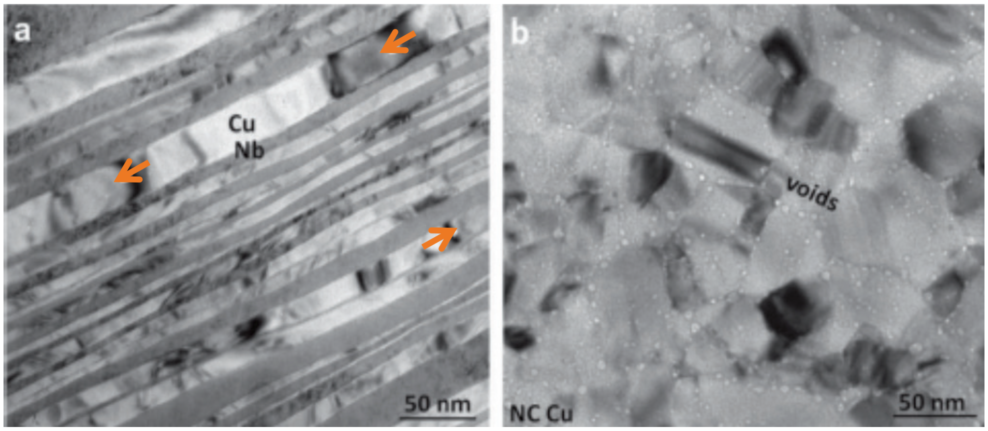


Figure 25. (a) Cu-Nb composites with 20 nm individual layer thickness are nearly void-free after helium ion irradiation at 450°C to 3 dpa. Arrows indicate small, isolated voids in the thicker copper layers. (b) Irradiation damage and grain growth were observed in nanocrystalline copper under identical conditions. | Images courtesy of Massachusetts Institute of Technology, W. Han, Design of radiation tolerant materials via interface engineering, *Adv. Mater.*, 2013, 25, 6975–6979

To gain understanding of damage occurring at solid/solid interfaces requires the ability to characterize materials across broad time and length scales. The recent development of new experimental characterization techniques has enabled ultrahigh–spatial-resolution imaging and spectroscopy and provides new avenues to investigate the fundamentals of solid/solid interfaces. Beyond 2D characterization of model interfaces, 3D imaging and chemical mapping using transmission electron microscopy (TEM) and atom probe tomography (APT) provide unique information regarding the inherently complex structure and chemistry of solid/solid interfaces and radiation-induced solute redistribution and precipitation. [Dong 2013; Marquis 2010; Ardell and Bellon 2016] APT and fast data processing permit detailed insight into the structure of these materials. The temporal dimension is also available through in situ experiments in coupled extremes—such as irradiation, controlled environment, and nano-mechanics—via TEM or synchrotron x-ray characterization. In situ environmental TEM provides a tool to reveal the effects of temperature and pressure on oxidation and corrosion mechanisms and rates. However, it should be noted there is a trade-off in that high-resolution techniques are generally also low volume; techniques are needed to bridge the spatial gap so the knowledge gained at high resolution can be extended to understand bulk behavior.

Parallel to the experimental advances, new computational approaches have also become available to quantify interface structures, discover new mechanisms, and elucidate defects and interactions across multiple length and time scales. [Vattre 2014; Bai 2010; Choudhury 2015; Dholabhai et al. 2014]

Scientific Challenges and Opportunities

Solid/fluid interfaces

Understanding the mechanisms at solid/fluid interfaces presents enormous challenges because of the higher temperatures, radiation doses, and pressures expected in future nuclear reactor concepts and systems. Radiolysis and charge transfer at interfaces under extreme conditions generate reactive intermediates that can lead to changes in the coolant chemistry, dissolution of the solid into the fluid, corrosion of the buried interfaces (metal-oxide and intergranular interfaces), erosion and defect formation on the surface, material restructuring and/or elemental segregation that changes the surface reactivity, and damage to protective layers or coatings [Tupin 2015] (Figure 26).

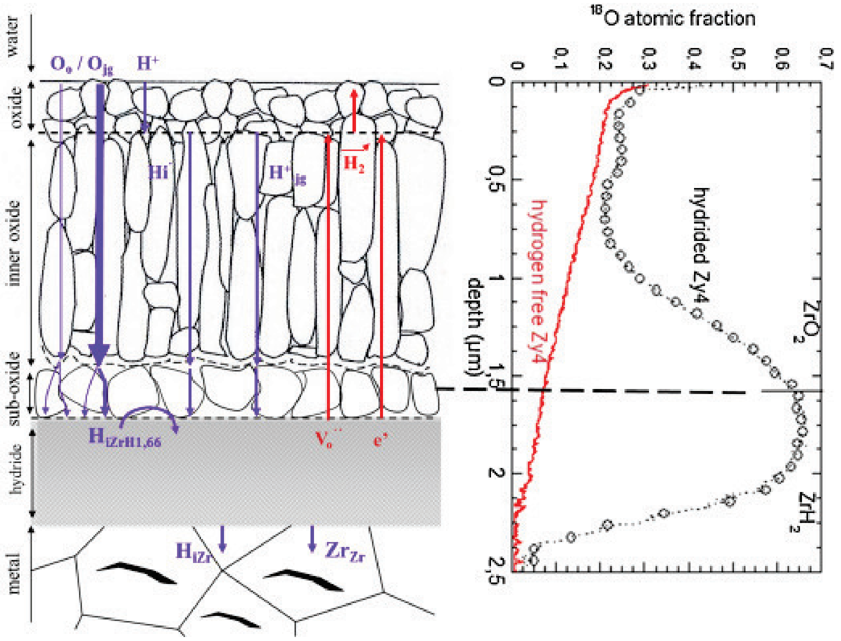


Figure 26. Schematic illustrating the mechanism of corrosion of zirconium hydride and impact of precipitated hydrides on Zircaloy-4 corrosion behavior. | Reprinted from *Corros. Sci.*, 98, M. Tupin et al., Mechanism of corrosion of zirconium hydride and impact of precipitated hydrides on the Zircaloy-4 corrosion behavior, 478–493, copyright 2015, with permission from Elsevier

The scientific challenges include

- Understanding and quantifying how radiolytic energy, charge, and heat are transported at solid/fluid and fluid/fluid interfaces (e.g., metals, oxides, salts, bubbles, and particles of many kinds)
- The roles defects play in solid/fluid interface reactivity and how they evolve in high-radiation and high-temperature environments
- How to design coatings and meta-materials that can control interfacial reactivity under extreme conditions

- The development of integrated mechanistic models leading to coherent design of complementary and compatible materials and fluids (e.g., equipment and coolant)
- The use of interfacial effects to increase the heat capacity and fuel carrying capacity of molten salts.

Interfacial phenomena must be probed across broad spatial and temporal scales relevant to energy transfer and chemical reactivity, using advanced and emerging experimental spectroscopic, imaging, and scattering capabilities. New experimental techniques that achieve ultrafast time resolution and ultrahigh spatial resolution are rapidly progressing. For example, interface-specific detection methods such as grazing-incidence scattering, and nonlinear optical techniques that exploit the asymmetry of interfaces have been successful in aiding the understanding of interfacial structure and reactivity.

However, new in situ characterization methods are needed to characterize these materials and chemical processes in real time under the extreme conditions expected in future nuclear reactors. These new analytical tools are needed to examine chemical and physical processes on the surfaces of nanoparticles, at buried interfaces, selectively within phase domains (solid, liquid, gas, and by composition), and in 3D on the meso and macro scales—all with high spatial and time resolution and chemical specificity. These advanced experimental techniques will require close cooperation with theory and data analytics to interpret the observed phenomena, predict spectroscopic and structural fingerprints for detection and assignment, and suggest specific targets for experimental investigation.

Integrated mechanistic models for complex interfacial processes across the atomic-, nano-, and mesoscales are required for the design of complementary and compatible reactor materials and coolants. On the atomic scale, quantum calculations and MD simulations can be used to predict energetics and model nonequilibrium phenomena, multi-state dynamics, and reactivity. An important challenge will be to accurately describe radiation-driven reactions at interfaces. On the scale of nanometers, modeling is needed to understand the assembly and evolution of structural features such as the formation of particles, layers, and segregated phases, and the forces and dynamics that drive their organization into larger-scale structures. Results from quantum calculations and modeling must be reliably embedded into models to predict aging behavior and the evolution of material properties over longer time and length scales. The development and integration of more powerful computational tools (electronic structure, embedded methods, multiscale simulations, and machine learning) should lead to the mechanism-based design of materials and interfaces that provide control over interfacial reactivity under the demanding conditions of next-generation reactors.

Solid/solid interfaces

A key challenge in mastering the radiation tolerance of fuels and structural materials is to obtain a fundamental understanding of the unit mechanisms of defect interactions at internal interfaces, such as grain and interphase boundaries, as a function of interface chemistry and structure. Once these unit mechanisms are elucidated, two significant new areas of science emerge:

1. Understanding and predicting the behavior of ensembles of randomly distributed interfaces within a hierarchical microstructure
2. Designing *adaptive* internal interfaces that heal rather than nucleate and propagate damage

Multiscale simulations, informed by physical mechanisms from unit to collective response, are required to develop predictive models of material behavior for increased efficiency, decreased performance margins, and reduced safety concerns in future nuclear systems.

The fundamental insights gained from the unit mechanism and ensemble studies can be used to creatively design new material microstructures that provide enhanced properties satisfying the operational parameters of the proposed future nuclear system technologies. As the field advances to mechanism-based design, increasingly complex aspects of the reactor environment can be modeled in combinations of controlled environments.

Many concurrent extreme conditions will be present in any future reactor, including displacement damage, introduction of transmutants, elevated temperatures, large temperature gradients and temperature changes, mechanical loads, and/or other types of harsh environments. Combinations of these stressors may result in synergistic effects that may be catastrophic to the essential properties of the advanced materials chosen. Some of these responses have been highlighted in conventional materials systems, such as radiation-induced segregation, stress corrosion cracking, shadow corrosion, and crud. However, little work has been done to investigate the roles of various grain boundary types, interface natures, or surface structures in the responses to the extreme environments that will be present in advanced reactors. This deficiency is further compounded as material systems with nanocrystalline, nanolayer, or nano-dispersion structures are considered, as even less is known about the responses of ensembles of interfaces to these complex overlapping environments. [Han 2013; Demkowicz 2010; Beyerlein 2013; Wu 2016; Parish 2017; Stan 2017; Tupin 2015] Combining state-of-the-art multiscale modeling with in situ experimental testing will greatly enhance understanding of the physical and chemical processes that occur at these intertwined interfaces, boundaries, and surfaces in extreme reactor environments. Given the complexity of the alloy compositions and chemical heterogeneities (e.g., metal-oxide) at interfaces, advanced computational approaches such as machine learning are needed to elucidate the information contained in these data [Xue 2016].

From the fundamental knowledge of kinetics at interfaces, defect interactions, stress development, structure, and chemistry, and considering the elusive role of impurities, two major scientific questions emerge:

1. How do we design materials with hierarchical structures of interfaces to produce tailored responses at irradiation extremes?
2. How do we accelerate the development of novel interface-enabled radiation-resilient materials using advanced, experimentally validated, physics-based computational models?

Conclusion

Understanding the wide range of physical and chemical processes that occur at surface (solid/fluid) and buried (solid/solid) interfaces that are proposed for the variety of advanced reactor concepts is a daunting challenge. All of the proposed future nuclear energy technologies involve harsh environments (high radiation dose, high temperature, mechanical strain, and corrosive environments) beyond present experience that will require a new generation of materials designed for tailored responses. Interfaces will have critical impacts on the performance, safety margins, and operational lifetimes of next-generation reactors. To predict materials evolution and degradation, a fundamental understanding of the reaction mechanisms active at the surfaces of and within materials in a complex combination of environments is critically needed. This knowledge will be enabled through advancements in characterization and computation tools that will provide detailed insights into material and coolant degradation at interfaces across broad time and length scales. For example, advancements in combined in situ electron microscopy, APT, and synchrotron and neutron scattering techniques, coupled with multiscale modeling, could provide ways to map out the 3D evolution of interfaces under the harsh environments proposed for advanced nuclear reactors.

Once a fundamental understanding of the mechanisms of the myriad chemical and physical processes that occur at interfaces is achieved, this knowledge will catalyze the development of a new generation of materials designed to perform in the extreme environments anticipated in future nuclear energy systems. Recent advancements in experimental tools and computational methods provide confidence that fundamental research will succeed in understanding the evolution of surfaces and buried interfaces; develop science-based, experimentally validated computational models; and subsequently design tailored materials for the advancement of future nuclear energy technologies.

Panel C: Understanding Behavior at Coupled Extremes

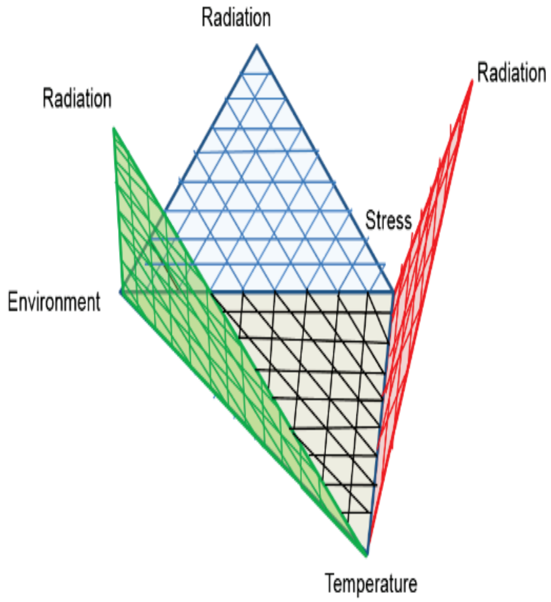


Figure 27. Illustration of the multidimensional aspects of materials degradation in nuclear environments. | Image courtesy of Peter Hosemann, University of California–Berkeley

Understanding the behavior of materials in the complex environment of an operating reactor is a daunting scientific challenge. Even for mature technologies, such as present-day light water reactors that generate approximately 20% of US electricity, [IAEA 2017] there remains a huge gap in knowledge that inhibits our ability to understand and mitigate the phenomena that degrade these systems. The extreme environments that will be encountered in future nuclear energy systems, which will use nonaqueous coolants and operate at extreme conditions, will present an entirely new set of challenges beyond those encountered in existing reactors. It is critical to understand the full range of effects that operating conditions can have on materials used in future nuclear systems. [OECD 2011] To achieve this understanding requires fundamental research that examines the behavior of materials systems—from the atomic to the macroscopic scale—under the full range of extreme conditions relevant to future nuclear systems. Figure 27 illustrates the multidimensional nature of materials degradation under such extreme conditions as a quadruple phase diagram.

Current Status and Recent Advances

There are many known routes that can degrade materials and eventually lead to failure—extremes in temperature, stress, and corrosion, among others—and each can involve complex systems of physical and chemical processes. The combination of extreme environments encountered in a nuclear reactor can alter these processes, leading to an even more complex system of degradation pathways. Radiation-induced defects in the solid can lead to the formation of chemical and structural inhomogeneities (e.g., precipitates, defect clusters), as well as to segregation of elements to sinks (e.g., grain boundaries and interfaces). These microchemical changes can in turn have a significant impact on corrosion, e.g., by depleting grain boundaries of corrosion-suppressing elements, through the effect of stress on chemical reactions, by changing the local electrochemical potential. For example, at interfaces, corrosion is a major contributor to the degradation of materials. Corrosion is a collection of complex processes that may involve liquid/solid interfacial charge transfer, dissolution of metal surfaces, and/or adsorption-induced processes. However, these processes may vary depending upon the specific environment encountered. For example, corrosion in localized spaces, such as cracks and pits, with high surface-to-volume ratios may exhibit different chemistries from those of planar surfaces. This situation becomes more complicated when protective surfaces are used, as in the case of a pressurized water reactor. The buildup of surface oxide films protects the underlying metal against corrosion, and characterization studies have provided insight into the nature of the passive film and its growth (Figure 28). At the atomic level, this involves the interfacial transfer of metal cations, which induce significant changes in the physical and (electro-)

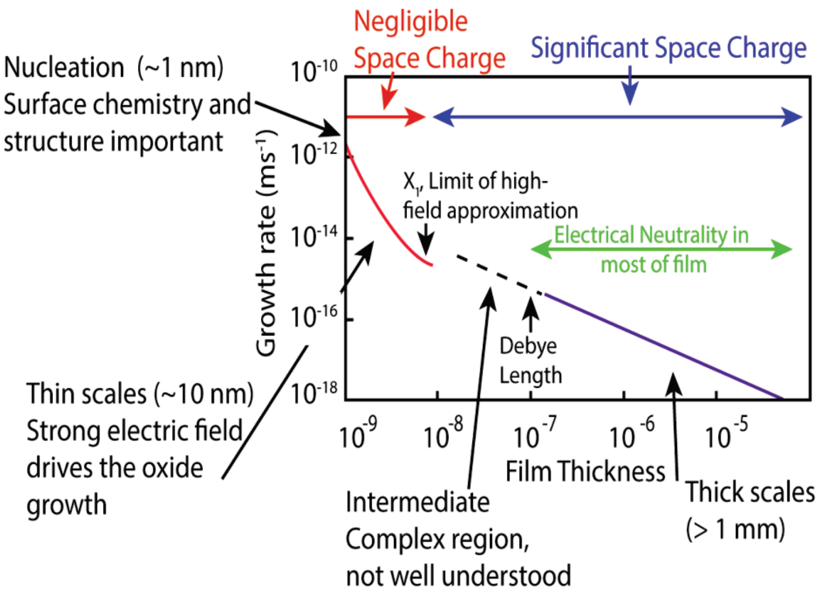


Figure 28. Oxide layer growth kinetics as a function of passive film thickness. 24 Caberra and Mott theory applies for films thinner than X_1 and Wagner theory applies for films thicker than the Debye length and X_1. | Reprinted with permission from A. Atkinson, Transport processes during the growth of oxide films at elevated temperature, *Rev. Mod. Phys.* 57, 437, April 1, 1985. Copyright 1985 by the American Physical Society

chemical nature of the interfacial region with time. Concentration gradients of dissolved metal cations may develop as corrosion progresses. The dissolution of metal cations can lead to the formation of new dissolved metal species (e.g., with varying valence and coordination) or precipitated structures, such as dispersed colloid particles, gelatinous solids, crystalline grains, or thin films. Further complications arise if the chemical and physical properties of the solution and the oxide phase are not uniform or stationary. These changes in the interfacial region, in turn, can strongly affect the rate of redox reactions and alter corrosion pathways.

These complex corrosion processes may become even more complicated in the presence of an intense neutron radiation field. Currently, a conventional 3 GWth reactor at full power experiences a neutron radiation dose rate of ~400–500 MGy/h in the vicinity of the core. This constant source of energy results not only in direct changes in the solid material but also in the radiolysis of the coolant, causing the formation of reactive species that further contribute to material degradation. Currently, there is an appreciable understanding of the various species that are formed in irradiated water [Buxton et al. 1988]; and the extrapolation of this chemistry from neutral, low-temperature water to reactor conditions has also been achieved. [Elliot and Bartels 2009] However, our understanding of similar processes in nonaqueous coolants, including gases, liquid metals, and molten salts, required for the next generation of advanced nuclear energy systems that will operate under more extreme environmental conditions is still in its infancy.

Radiation can decompose coolant molecules into redox-active species that may strongly influence metal oxidation and particle growth. Corrosion kinetics and radiolysis kinetics are highly interdependent. Existing models based on water-cooled reactors are 2D (time, oxide thickness); but in practice, the process is inhomogeneous in 3 dimensions, with multiple phases and structures at the nanoscale. The quantitative effect of radiolysis on corrosion varies depending on the physical and chemical properties of the solution. Examples include the effect of γ-radiation on carbon steel, known to vary considerably depending on pH. [Daub et al. 2011] Further, enhanced corrosion under radiation has also been observed on zirconium alloys. Zirconium samples under irradiation grow significantly thicker oxide layers than do unirradiated samples. Similar synergistic effects include hydrogen, helium, and displacement damage leading to enhanced swelling (Figure 29); radiation-enhanced creep; or fretting issues. These are examples of coupled phenomena that lead to accelerated materials degradation, compared with a 1D problem.

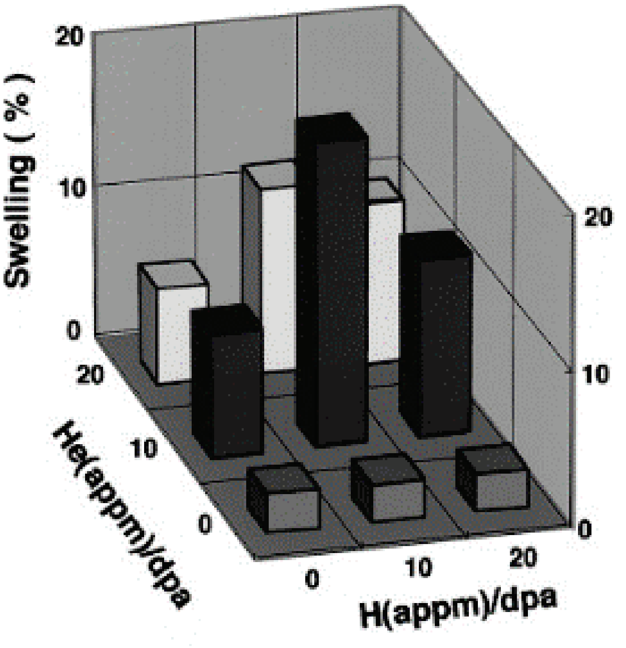


Figure 29. Synergistic effects of helium and hydrogen ion beam irradiation leading to swelling. | Reprinted from *J. Nucl. Mater.*, 283–287, Part 1, N. Sekimura et al., Synergistic effects of hydrogen and helium on microstructural evolution in vanadium alloys by triple ion beam irradiation, 224–228, copyright 2000, with permission from Elsevier

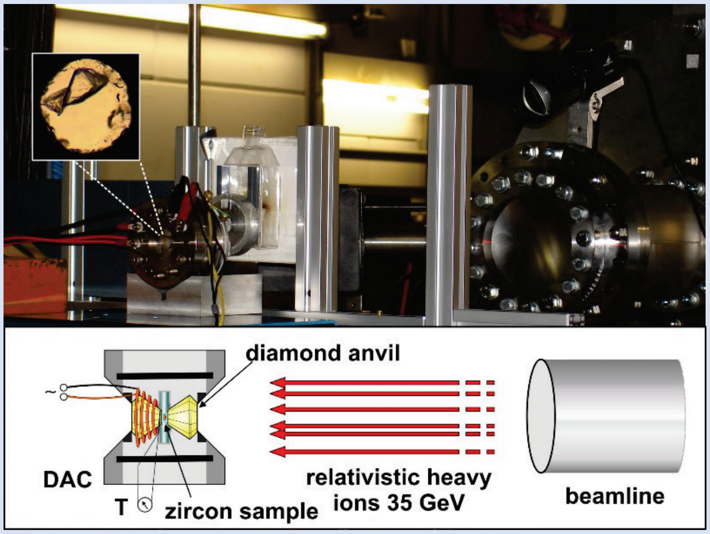
Individually, each extreme—radiation, corrosion, stress, temperature, among others—poses its own challenge to an understanding of the reactor environment. However, it is the combined effects of coupled extremes that are particularly challenging to understand and that pose a major scientific challenge (see the sidebar "Coupling Three Extremes: High Pressure, Energetic Ion Irradiation, and High Temperature"). One example of coupled environments includes the simultaneous effects of chemical environment and stress. Flow-induced vibrations and dimensional changes of materials under irradiation can lead to stresses, which may result in undesirable wear of materials. This coupling of mechanical wear and chemical corrosion is known as tribocorrosion, [Beaudouin et al. 2006] fretting-corrosion, [Chitty et al. 2011] or erosion-corrosion. [Davis and Frawley 2009; Jana and Stack 2005; Srinivasa et al. 2008; Stack et al. 2010; Long et al. 2017; Xue et al. 2014] Tribocorrosion, fretting fatigue, and wear problems have major economic and safety impacts for the nuclear industry. Flow-induced vibration, component-to-component contact, and corrosion processes will also occur in advanced nuclear energy systems that employ alternative coolants such as sodium, lead, helium, or molten salts, making tribocorrosion and wear an important issue to understand. Another example of important phenomena that result from the coupling of stress to the chemical environment is environmentally assisted cracking. Harsh environments may produce vacancies by a number of mechanisms, which can eventually lead to cracking. This issue can be expected to become worse under the extreme operating conditions that are anticipated in future nuclear energy systems. [Arioka 2014; Arioka et al. 2016] There is only a limited fundamental understanding of the behavior of materials under such conditions.

Proposed advanced nuclear energy concepts will use nonaqueous coolants and may operate at much higher temperatures, pressures, and radiation dose rates than the current generation of light water reactors. Thus, the multidimensional challenges discussed present an even more formidable challenge in these future reactor systems. These new coolants will interact with structural materials, presenting new types of corrosion processes. Thus, it is critical to develop a fundamental knowledge of the full range of phenomena governing coolant/material interactions to enable the design of next-generation nuclear reactor systems.

Corrosion of materials exposed to molten salts can be exacerbated by irradiation, just as in the case of aqueous coolants; accelerated corrosion has been reported even if the irradiation of the solid material took place before its exposure to molten salts. [Li et al. 2017; Zhu et al. 2017] The effect of irradiation on the molten salts themselves is poorly understood; however, molten salt ions can be expected to be further transformed by radiation. For example, the fluoride ion present in a FLiBe salt can produce an F-radical and an electron. Because the molten salt is a conductive medium, these free electrons can react with a cation or a surface acting as an electron sink. The reactive F-radicals may combine to form F_2 (gas), interact with other ions and impurities, or interact with the wall material. In general, pure molten salts do not react with the wall materials; however, corrosive reactions can be catalyzed by the presence of impurities in the coolant, such as oxides and water. [IAEA 2009] Because the molten salt medium is often sparged with a reducing gas mixture that may contain H_2 and/or HF, the HF may accelerate corrosion if there is any oxygen or water still in the system. Adding radiation to this chemically complex environment compounds the issues and, at present, the combined effects of impurities and irradiation upon corrosion processes in these molten salt systems are unknown.

Coupling Three Extremes: High Pressure, Energetic Ion Irradiation, and High Temperature

Multiple extreme conditions have been coupled in the past to mimic the formation of fission tracks within Earth's interior by exposing natural zircon, at a pressure of 7.5 kbar and a temperature of 250°C, to a beam of relativistic heavy ions. [Lang et al. 2008] The approach is based on a recently developed method using swift heavy ions and a heatable diamond anvil cell (see photo at left). Pressure is created by squeezing two opposing diamond anvils against a sample chamber with an aperture (diameter ~0.5 mm) drilled in a steel gasket and filled with liquid as the pressure-transmitting medium. Heavy ions of relativistic kinetic energies (35 GeV), produced by one of the world's largest ion accelerators (GSI Helmholtz Center), are injected through one of the two anvils of a pressure cell into the pressurized sample. The high kinetic energy of the ion beam is required because it first must traverse the millimeter-thick diamond anvil of the high-pressure cell before reaching the pressurized sample. Temperature is maintained during irradiation by means of molybdenum heating wires wrapped around each diamond. The response of materials to coupled extremes can be dramatically different from the behavior under separately applied extremes. For example, the application of high pressure simultaneously with the deposition of large energy densities provides a new strategy for the formation and recovery of unique, high-pressure structures that are otherwise inaccessible. [Lang et al. 2009]



Photograph (top) and schematic illustration (bottom) of the irradiation experiment for exposing pressurized heated samples to a beam of relativistic heavy ions. The very small sample (300 µm in diameter and 40 µm thick) is enclosed in the diamond anvil cell. The inset displays the optical micrograph of a zircon crystal in the cell. For the irradiation, the cell is placed in air, 45 cm behind the beam line window. The schematic (not to scale) shows the details of the anvil cell, including the resistance heating coil (shown for only one anvil). | Reprinted from *Earth Planet. Sci. Lett.* 274, M. Lang et al., Fission tracks simulated by swift heavy ions at crustal pressures, 355–358, copyright 2008, with permission from Elsevier

Finally, how the reactor is operated (such as load following), can also lead to high stresses, adding another dimension of complexity in these extreme environments. These stresses are accommodated by dislocation slip, leading to formation of dislocation channels within the irradiated matrix. The intersection of these channels with grain boundaries can result in their being blocked, which causes an out-of-plane displacement that ruptures the protective oxide. [McMurtrey et al. 2015] This exposure of the bare metal to the coolant can initiate an irradiation-assisted stress corrosion-cracking event. What remains to be resolved is why cracking initiates at one blocked dislocation channel rather than at an adjacent one. Is it simply a stochastic event, or are there intrinsic local differences in the structure and composition of the grain boundary? Liquid metal embrittlement in heavy metal–cooled reactors is also known to exist; and the combined effects of stress, temperature, radiation, and salt environments are virtually unexplored. Based on studies in both irradiation-assisted stress corrosion cracking and liquid metal embrittlement, the composition as well as the structure of the grain boundaries has emerged as an area requiring atomistic-level understanding.

It can be seen from this discussion that there are substantial gaps in our knowledge that it is critical to resolve as we strive to meet the full potential of future nuclear energy systems. These challenges can be met only by developing a fundamental understanding of the myriad processes that occur under multiple extremes of radiation, stress, and heat in novel, nonaqueous systems.

Scientific Challenges and Opportunities

Understanding the dynamic and highly coupled processes that occur at material interfaces present under extreme conditions is crucial to the development of future nuclear energy systems. However, simple studies of materials and systems at a single given extreme will not be sufficient. For instance, in molten salt–cooled systems, corrosion is driven by dissolution of metallic elements into the salt, as no protective oxides can be formed. Chromium dissolution is a primary concern. Given that dissolution is faster along grain boundary pathways, because radiation changes grain boundary compositions as a result of radiation-induced segregation, the corrosion response is directly coupled to radiation as well as surface chemistry. Studies under coupled conditions can provide insight into the full complexity of interfacial reactions, transport phenomena, microstructural evolution, and material defect formation and propagation. This is because the effects resulting from the combination of radiation fields, high temperature, pressure, and stress may compound one another and yield processes and mechanisms that are active only when multiple extremes are concurrently studied (Figure 30).

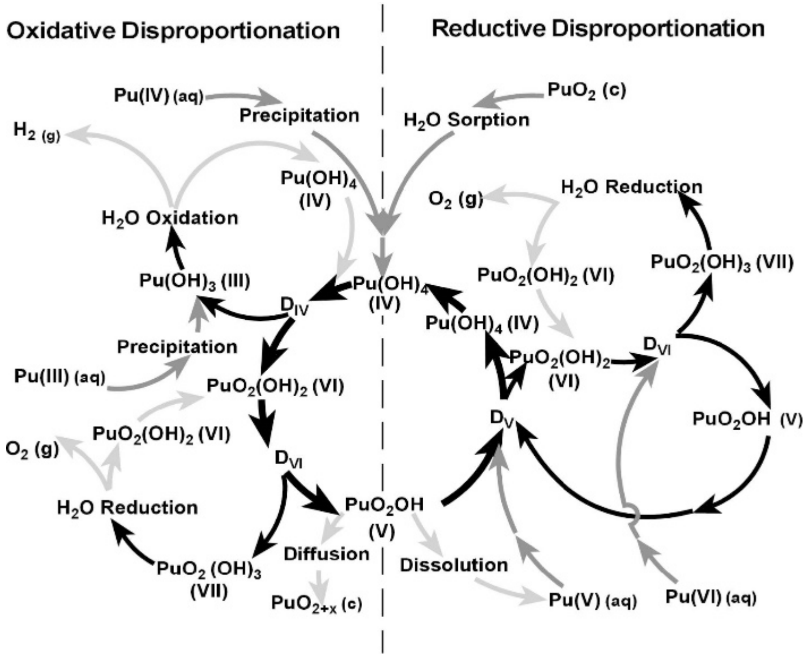


Figure 30. Illustration of a chemical system that may initially appear simple but is complicated by radiation and environmental effects. | Image courtesy of J. M. Haschke and W. J. Siekhaus, Lawrence Livermore National Laboratory

As these inextricably linked processes are unraveled, researchers will be challenged to develop new materials, interfaces, and multicomponent systems that survive in harsh, nonequilibrium environments where high-energy, transient species are present. Although most chemical analyses are currently performed by characterizing the molecules and materials before and after experiments in extreme conditions, it is a challenge to understand the changes in the sample *during* the experiment. These experiments will be facilitated by the development of computational models that can provided additional insight into the complexity of the coupled environments to accurately predict material characteristics across different length and time scales (Figure 31).

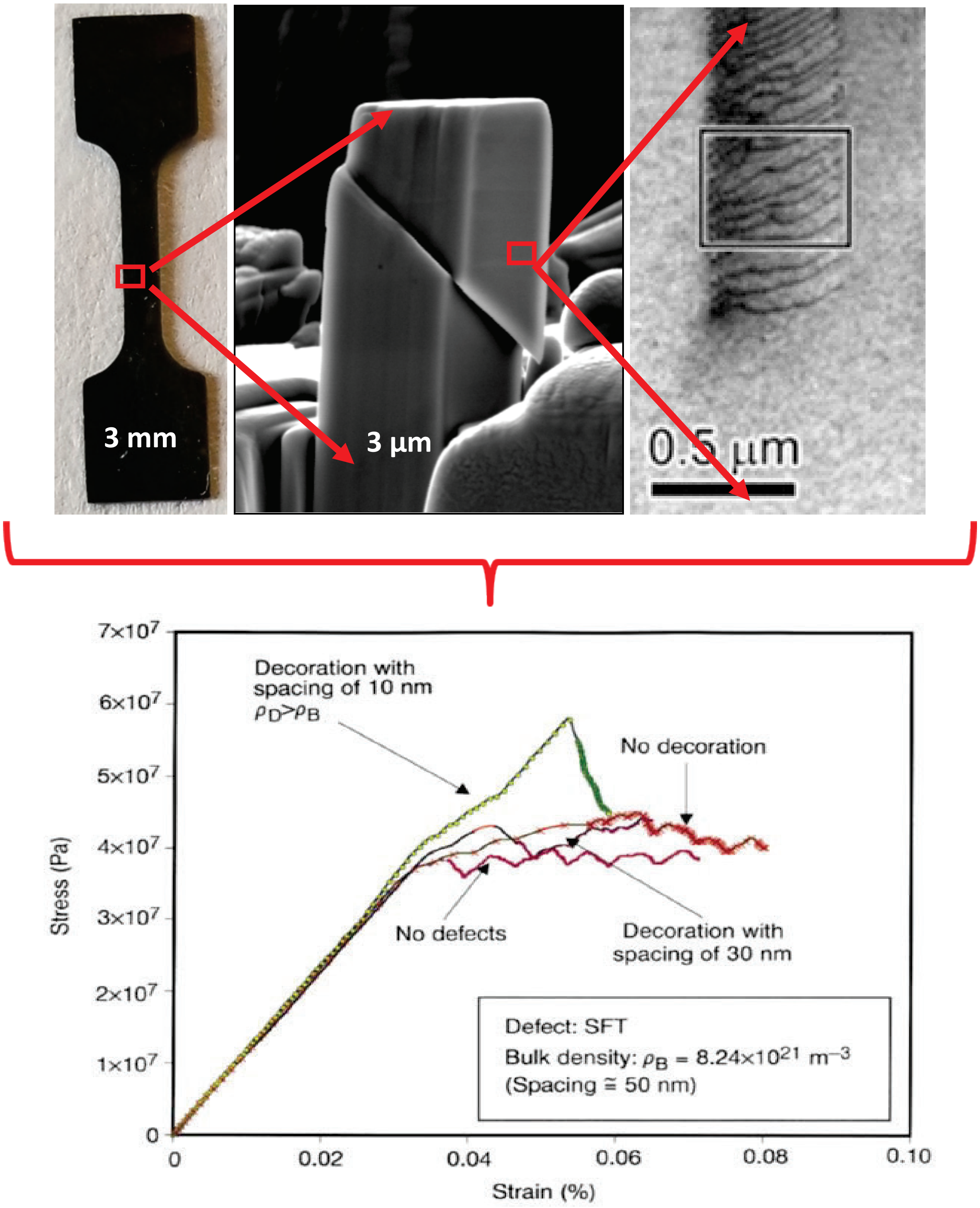


Figure 31. (Top) Example of the experimental multi–length scale observation of localized failure of irradiated materials. | Reprinted by permission from Macmillan Publishers Ltd: *J. Nucl. Mater.*, A. Reichardt et al., Nanoindentation and in situ microcompression in different dose regimes of proton beam irradiated 303 SS, 486, 323–331, copyright 2017; Reprinted from *Science Direct* 43(11), J. Kacher et al. In situ and tomographic observations of defect free channel formation in ion irradiated stainless steels, 1099, copyright 2012, with permission from Elsevier (Bottom) Modeling efforts attempt to reproduce this behavior. T. Diaz de la Rubia et al. 2000. "Multiscale modelling of plastic flow localization in irradiated materials," *Nature*, 406, 871–874

Given the extreme conditions anticipated for future nuclear energy systems, a new generation of materials are needed that are capable of operating reliably for long periods of time. To facilitate the design of these materials, there is an urgent need to understand the coupled effects of these extreme environments. There are complementary types of research that will help to fulfill this need, including new experimental techniques to couple these extremes, new characterization tools to collect data in situ, and accurate models to simulate and ultimately predict materials properties and characteristics

New characterization methods are needed to provide an improved understanding of the complex and linked chemical and physical processes that ultimately lead to degradation of materials, both structural materials and coolants, under realistic conditions. This understanding will ultimately provide a knowledge base to allow for the targeted development of materials that retain their properties and resist degradation under the harsh environments of future nuclear systems. In particular, there is a need to develop multi-modal techniques that can provide multiple dimensions of information on a single sample in situ. There is also a need to integrate time-resolved spectroscopic and imaging techniques (e.g., microscopy, x-ray, neutrons) with multiscale/integrated-scale modeling and in situ data analysis and visualization. Doing so will allow for the design and implementation of experiments with higher spatial and temporal resolutions than are available to each individual technique. Advances in data analytics and machine learning techniques can allow for efficient reconstructions from imaging and x-ray or neutron scattering data, which can be imported to create atomistic or continuum models. Such approaches will enable the development of “experimentally informed models,” thus bridging the gap between modeling and experimentally probed structures and conditions.

To model materials phenomena and properties at coupled extremes, there is an urgent need to combine the accuracy and flexibility of electronic structure calculations with the speed of classical potentials by merging and exploiting the best insights from the fields of machine learning, advanced optimization, and atomistic simulations. There is a need to develop flexible atomistic potential models that can describe many real important cases, such as nonstoichiometric defect formation, distributions of defects that include possible clustering or accumulation at surfaces or interfaces, charge and defect migration across interfaces, the effects of doping, and finite-size effects in thin films. In particular, there is a need to move beyond the fitting of specific data sets to reproduce specific properties that are valid only at equilibrium conditions, to fitting vast and diverse data sets obtained from first principles and experiments. Model machine learning algorithms, such as deep learning and genetic algorithms, are needed for enhanced sampling of training data with density functional theory and experimental inputs. There is a need to leverage state-of-the-art advances in model-building algorithms—such as genetic algorithms, compressive sensing, and deep neural networks—to describe scenarios that deviate far from equilibrium.

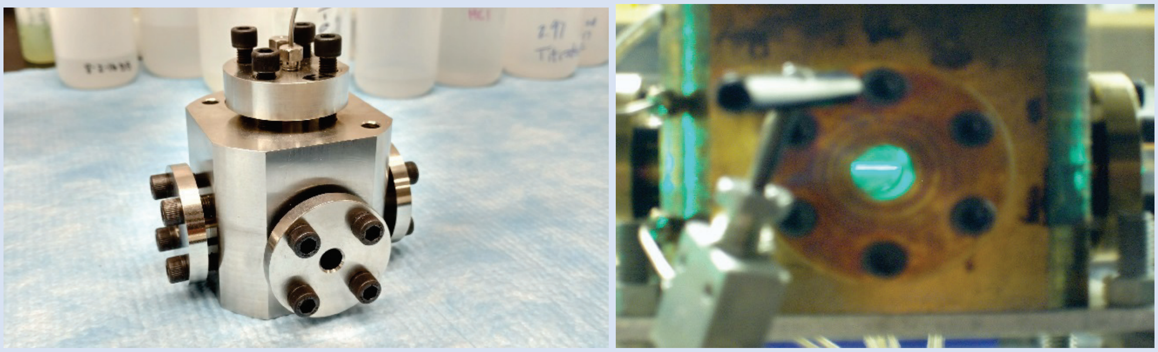
Multiscale modeling and multidisciplinary research have been the conventional paradigms for some years. But for a problem as complex as corrosion under irradiation, stress, and other nonlinear fields, researchers need to step beyond the conventional paradigms. There is a compelling interest in an integrated approach that crosses the barriers of specialization and in which theory and experiment are equal partners. Theory needs to move beyond mere replication of experiments to computation that can inform the direction of targeted experiments; and, in parallel, the experiments need to inform what classes of models and theories need to be explored. For example, phase field models of kinetics at interfaces need to be coupled with in situ measurements such as environmental electron microscopy. These need to be cross-referenced to ab initio calculations of key thermodynamic drivers, such as the activation energy of point defect migration in radiation and stress fields and the dependence of surface free energies on chemisorbed species from the external environment. This approach will allow elucidation of the fundamental mechanisms of materials transformation under extreme conditions. Further, to achieve mechanistic understanding, molecular dynamics computational experiments using potentials generated from higher-level first principles methods of nonequilibrium structures need to be combined with structural probes—such as x-ray scattering, and chemical probes—such as x-ray photoelectron spectroscopy and electron energy loss spectroscopy (see the sidebar "Coupling Three Extremes with Analytical Spectroscopy").

The integration of new characterization techniques during experiments at coupled extremes, and more accurate modeling, will improve our understanding of the processes in nonequilibrium kinetics/thermodynamics relevant to interface chemistry. This should be realized through a quantitative understanding of the effects of solution conditions coupled with radiation fields to ultimately revolutionize methods of assessing reactor structural materials, waste storage, disposal containers, and emergency preparedness.

Coupling Three Extremes with Analytical Spectroscopy

In situ and operando analytical techniques are necessary to fully understand chemical reactions that occur under coupled extreme conditions. Pre- and post-sample analysis will not always provide the same information as an examination conducted directly in the extreme environment. Yet the technique itself must survive the extreme conditions as well. An example is provided by the use of laser spectroscopy for the examination of reactions in supercritical water. In this work, a short-pulse pump 266 nm YAG laser and a continuous low-power probe argon ion laser beam were both focused onto a supercritical water cell. [Rodriguez et al. 2007] They produced a thermal lensing signal with a strength that could be maximized by changing the overlap of the two beams. Despite a very significant mirage effect due to thermal gradients in the cell and absorption by the water itself, the thermal lensing signal strength for aqueous benzoic acid in supercritical water was found to be linear, with a concentration in the sub-millimolar range. The supercritical water cell was machined from a solid block of 316 stainless steel (photo on left) with an internal volume of 12 mL.

Although only two windows were necessary to perform the analytical work described, [Rodriguez et al. 2007] an arrangement of the five sapphire windows allowed for additional experiments using laser excitation coupled with fluorescence measurements, or e-beam irradiation of the sample coupled with optical measurements. The windows were sealed with gold gaskets. The cell was heated using five separate cartridge heaters, and the temperature was measured by a thermocouple and controlled to within 1° by adjusting the current to the heaters. The cell pressure was maintained using a solution that was pumped into the cell through a stainless steel line preheated to the desired temperature using an Isco syringe pump. Thus, analytical measurements under supercritical water pressures and temperatures were possible, and the setup provided an additional capability to simultaneously irradiate the sample with an electron beam. The photo at right shows the laser transiting the cell while under temperature and pressure, as viewed through an orthogonal window.



(Left) Supercritical water cell equipped with five sapphire windows allowing simultaneous irradiation and spectroscopy. (Right) Laser light transiting the cell while it is under temperature and pressure. | Images courtesy of Bruce Mincher, Idaho National Laboratory

Conclusion

A major goal in research in *understanding behavior at coupled extremes* is to develop a deep understanding of the synergistic effects among the radiation fields, temperatures, static and dynamic stresses, and environments to which a material can be exposed in conventional and advanced reactor systems. This effort will be the basis for underlying theory-based models that can be benchmarked against well-defined experiments unifying those conditions. The coupled nature of these harsh environments will necessitate the development of new experimental techniques that can examine a range of scales in time and space, and characterization methods to perform in situ measurements of the system. Furthermore, an integrated approach to modeling and experiments is necessary, as it will facilitate a better understanding both of the extensive data currently available from operating reactors and of future advanced energy systems, enabled by modern data mining and data extraction by modern algorithms. These models need to progress toward a continuous integrated scale approach to predict macroscale effects based on atomic-nano-, or micro-scale processes.

Among the important research questions that such techniques will answer are these:

- What is the role of radiation in corrosion?
- What is the role of stress in the fracture of irradiated alloys?
- What is the influence of aqueous and/or nonaqueous coolants in stress corrosion cracking?

Such an integrated approach promises exciting opportunities to further a fundamental understanding of the chemistry and materials science that occurs in the extreme environments that will be created future nuclear energy systems.

Panel D: Design and Discovery of Structural Materials and Solid Fuels

The realization of future nuclear energy systems will require accelerated and robust means to master the discovery and design of structural materials and solid fuels stable for use in extreme conditions. Such capabilities are not yet available but will emerge from enabling fundamental research on key materials and chemical processes that takes advantage of advances in theory, computation, experimental techniques, synthesis, and processing.

At least six types of Generation IV nuclear reactor concepts are at various stages of development. [Busby et al. 2017] All of the designs aim for much higher operating temperatures and higher burnup of fuels than current reactors. Materials will need to withstand extreme conditions of radiation flux, temperature, corrosion, and strain over unprecedented timescales. Insights into and approaches to the discovery of new materials and related phenomena must be pursued at a level sufficiently fundamental to establish realistic physical mechanisms as the basis for accurate modeling and simulation frameworks. Robust materials design rules and enabling synthesis and processing routes can then be established.

The past decade has seen impressive advances in the theory and modeling of structures and processes; profound progress in the computational and experimental sciences; the emergence of the Materials Genome Initiative (MGI; NSTC 2014; https://www.mgi.gov/) and other, related accelerated development approaches [Jain et al. 2013; Kuehmann and Olson 2009; Curtarolo et al. 2013]; and the genesis and improvement of synthesis and processing methods. [DOE 2007; DOE 2016] Holistically, these advances provide many opportunities to seek and perfect design strategies for the materials/fuels needed for future reactors. The capabilities to discover and design materials specifically tailored for advanced nuclear energy applications require further development of fundamental knowledge of structural, chemical and materials processes that underlie synthesis, processing, and design. Powerful methods to probe matter at sufficiently resolved time and length scales will be enabling. Progress will rely on verified predictive mechanistic models of materials to ensure tight integration among experimentation, theory, and simulation and the use of advanced methods of data synthesis and machine learning.

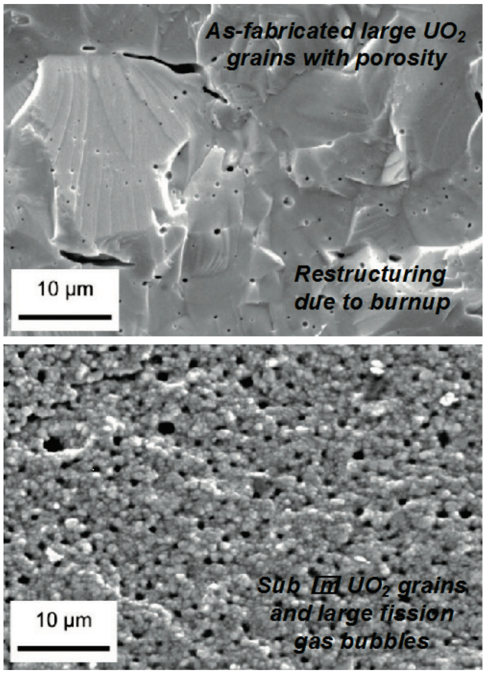


Figure 32. Illustration of microstructural changes in traditional fuel (UO_2) that defy current predictive capability. | Reprinted from *Mater. Today*, V. Rondinella et al., The high burn-up structure in nuclear fuel, 24–32, copyright 2010, with permission from Elsevier

Current Status and Recent Advances

The complex evolution of nuclear fuel (typically UO_2 in the current fleet of reactors) arises from its changing chemical composition, radiation-induced microstructural changes, and high thermal gradients. [Olander 1976; Olander 2009; Zinkle and Was 2013] During reactor operation, the generation of fission and activation products and the formation of transuranium elements result in the incorporation of one-third of the elements of the periodic table in the fuel. These are distributed over gas bubbles, in metallic and oxide precipitates, in solid solution in UO_2, and in other forms. Because of this incorporation and the other processes, fuel undergoes vast changes in grain size, grain boundaries, and the introduction of new interfaces (Figure 32). Furthermore, phonon transport is altered, leading to changes in the fuel temperature profiles.

Proposed solid fuels include oxides, nitrides, and carbides of the actinides Th, U, or Pu. [Olander 2009] The distribution of fission products and transuranic elements strongly depends upon the initial form of the fuel, the chemical properties of the fuel matrix, and cladding design and composition. Some fuels retain gaseous fission products at high temperature, whereas others release them. Although UO_2 fuel has been used for decades, the detailed understanding of and rigorous modeling approaches for its in-reactor evolution lack many of the mechanistic underpinnings, insights, and approaches needed for efficient design of new fuels. For example, at the atomic-scale level of modeling, extensive work has focused on individual species of fission products, their energetics, and how the fission product moves and interacts with extended defects such as grain boundaries. However, the computational framework for modeling the full multicomponent system, including all of the fission products and microstructure evolution, remains to be developed. Furthermore, the combination of high irradiation dose, fission product buildup, and low temperatures that limit defect mobility results in the formation of a high-burnup structure (HBS) on the periphery of light water reactor fuel pellets. [Zinkle and Was 2013; Bleiberg et al. 1963; Rodinella and Wiss 2010; Matze and Kinoshita 1007] An understanding is needed of some individual processes (e.g., resolution of bubbles [Olander and Wongsawaeng 2006) and the overall process of HBS formation. Insight into the microstructural evolution of HBS will further enable the development of predictive design strategies for new fuels.

The interaction of neutrons with structural components in the fission core results in radiation damage ranging from tens to hundreds of dpa. [Zinkle and Was 2013] High temperatures, thermal gradients, and radiation damage synergistically combine into a particularly extreme environment with respect to materials degradation. Radiation creates high concentrations of defects in materials, far beyond those under thermal equilibria, and these migrate and drive microstructural evolution processes. Microstructural evolution and thermal and mechanical loads result in high stresses that alter the materials and often compromise their integrity. These harsh conditions also are influenced by the chemistry of the heat transfer medium (coolant) and, through interfacial processes, cause undesirable effects on solid fuels and structural materials in fission power systems.

Obviously, robust design of nuclear materials requires the ability to rigorously predict the effects of radiation on the structure and hence the properties of materials. However, despite considerable advances made both theoretically and in computer simulation, there remains a need to incorporate, in a physically realistic way, all of the processes and mechanisms that occur during irradiation. For example, void swelling occurs in metals at doses >10 dpa, at temperatures within 0.3–0.6 of the typical alloy melting point, [Zinkle and Was 2013; Zinkle and Snead 2014] and is associated with an incubation period or a threshold. Although theories describing processes such as point defect generation, point defect transport, absorption of defects at sinks, and void growth due to vacancy or gas absorption at voids are separately available, an overall framework capable of predicting void swelling (and other defect processes) in different metals and microstructures is yet to be developed. Addressing this challenge presents an opportunity to accelerate the design and certification of new material systems. Applications of and advances in phase field modeling will be of great help in this regard, as will further progress in linking different time and length scales (multiscale modeling). The formulation of quantitative structure-property-mechanism relationships for the bulk and interfaces must be further developed and verified. This type of quantitative understanding will require modeling methods with improved accuracy to access the large time and length scales required for unraveling the collective phenomena necessary to the computational design of radiation-tolerant materials. [Demkowicz et al. 2010]

Presently, the ability to discover and design new structural materials and fuels is limited by the amount of accumulated knowledge based on prior experimental, analytical, and reactor operational experience. There have been materials advances and insights regarding qualitative design approaches, particularly in tailoring nanostructured features. [Zinkle and Snead 2014; Demkowicz et al. 2010; Odette et al. 2008] Furthermore, recent advances toward stabilizing nanostructures at high temperatures suggest that materials with finely tailored microstructures can be designed to withstand thermal and radiation extremes. [Chookajorn et al 2014; Miller et al. 2005] However, there are opportunities to improve the efficacy of discovery and design through investment in basic research that targets improvements in predictive capabilities and accelerated materials development. Improved fundamental understanding is needed in a number of areas, including high-temperature reaction pathways; phase formation; decay processes during absorption and scattering of neutrons; material interactions with fission products, gamma radiation, and self-decay, including HBS; and underlying structure-properties-processing-performance relationships (all discussed elsewhere in this report).

Scientific Challenges and Opportunities

It is widely agreed that the historical and current timeline for developing most new materials (on the order of 10–20 years) must be shortened to meet the continually increasing demands set by the performance, economic, environmental, and energy expectations for advanced technologies. Accelerated discovery and design of materials is therefore critical and was the major driving force for the MGI (https://www.mgi.gov/). For nuclear materials, including fuels, the development timeline based on the current state of the art is even longer. Therefore, contracting the time between discovery and materials deployment for future nuclear systems is essential. This effort logically starts with developing accelerated methods of discovery; of materials design, synthesis, and processing; and of validating the properties and performance of new compositions and structures.

The barriers to accelerating the materials development process for nuclear systems are scientific, technological, and regulatory in nature. Efforts to meet the scientific challenge will immensely aid in overcoming the other two barriers. Therefore, there is a need for greater fundamental knowledge of nuclear material behaviors based on a mechanistic understanding of the interplay of compositional modifications, defect formation, deformation, and dynamically changing microstructure and nanostructure/chemistry as they are exacerbated by extreme environments. In this context, the overarching scientific goal related to robust materials design rules must be a holistic understanding of materials and fuels behavior in nuclear energy environments to enable the specification of robust materials and fuels for radiation environments in a way that substantially shortens the traditional development cycle.

The goal is challenging, but it presents compelling opportunities to unravel basic material and chemical processes that will enable transformative advances in designing structural materials and solid fuels for future nuclear energy systems. This effort will naturally benefit from recent worldwide efforts to develop effective frameworks for accelerating materials discovery and design via advances in theoretical and simulation and in handling and analyzing large data sets. These approaches—often combining theory, modeling, and experiment—have been successful in developing functional materials for targeted applications (e.g., electrical energy storage devices [Ceder 2010] and a structural alloy for military aircraft landing gears [Olson et al. 2013]) much more quickly than is traditional for the respective material classes. These positive outcomes provide a clear motivation for conducting basic research to enable accelerated discovery and design of nuclear materials and fuels.

Current (and future) specific successes of materials discovery and design frameworks are rooted in the ability to calculate energetics and to fundamentally relate atomic and microscopic processes to desired/targeted macroscopic engineering properties. [Ceder 2010; Olson 2013] Typically, these atomic/micro-to-macro relationships are better established for functional materials (e.g., batteries, thermoelectrics, photovoltaics) than for structural materials and nuclear fuels. Computationally guided design of new structural alloys has been successful when the targeted properties could be directly related to specific microstructural characteristics. This was the case when in-depth scientific knowledge about hardening and strengthening mechanisms in steels was used to develop ferrous alloys for landing gear and armor applications. [Olson 2013; Saha and Olson 2007] Similarly, processing-structure-properties relationships are at the core of computationally based synthesis and processing of materials. [Brough et al. 2017] In all cases, these fundamental relationships form the foundation for effective high-throughput screening (computationally and experimentally) and predictive design approaches. Accordingly, such knowledge bases frame the present discussion of basic research needs to substantially reduce the time required to discover new compositions, structures, and processing routes and to design, develop, and produce materials for future nuclear energy systems.

Illustrating by examples, the following are possible research areas that are responsive to the basic research needs emanating from the scientific goal and opportunities.

Self-healing materials through control of sink strength and chemical complexity

Point defects and defect clusters are created homogeneously in a solid under irradiation and are eliminated or trapped at chemical or structural inhomogeneities. The buildup of sustained fluxes of excess point defects in irradiated alloys often leads to detrimental evolution of the microstructure and properties, including swelling, creep, and radiation-induced segregation and precipitation. Therefore, a promising design strategy for radiation-resistant materials is the introduction of a high density of sinks and traps for point defects and gas atoms.

Sinks can be efficient at absorbing and eliminating point defects. Atomistic simulations show their efficiency can be strongly affected by the interface structure of a sink, particularly the degree of coherency between the sink and the matrix. [Demkowicz et al. 2008] It is therefore necessary to measure sink efficiencies experimentally to validate atomistic models and assess the coherency for the interfaces present in irradiated alloys, which often depart from ideal. Past measurements were indirect and focused on voids or precipitate-denuded zones near extended sinks such as grain boundaries. [Han et al. 2012] New approaches are required; an example is the use of thin films with controlled microstructure [Mao et al. 2015] (Figure 33), particularly in combination with high-throughput computational screening. [Curtarolo et al. 2013] Direct measurements of 3D sink structures are particularly needed to elucidate the role of coherency, interfacial segregation, and elastic modulus in sink behavior. This schema will facilitate accelerated, computationally enabled design of nanoprecipitates or other nanoscale structural features with optimized sink strength.

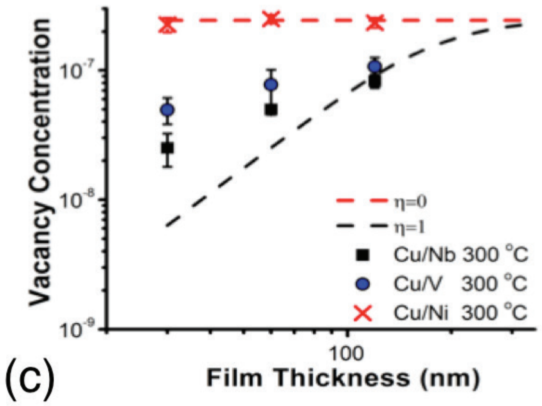


Figure 33. Sink efficiency η measured during 1.8 MeV Kr irradiations at 300°C for Cu/Nb, Cu/V, and Cu/Ni interfaces. The Cu/Nb interface is close to a perfect sink (η ≈ 1), Cu/Ni is close to a very poor sink (η ≈ 0). | Reprinted from *Acta Mater.* 82, S. Mao et al. Quantitative comparison of sink efficiency of Cu-Nb, Cu-V and Cu-Ni interfaces for point defects, 328–335, copyright 2015, with permission from Elsevier

Looking to future nuclear energy systems, it is desirable that materials be designed with microstructures/nanostructures that are stable under the thousands of dpa and extensive chemical evolution (up to 40% change in composition) that are experienced in solid fission fuels. Fission gas bubble mobility in a fuel may be reduced by incorporating sinks with species-specific chemical affinity. Understanding how to tailor the surface energy of the fuel to enhance sinks' gas retention inside smaller, higher-pressure bubbles is seen as a key to advanced design and synthesis. Incorporation of trapping sites (microstructural or chemical) for mobile radionuclides through advanced synthesis will be needed.

Recent progress in understanding energy dissipation and the initial stages of defect evolution as controlled by the degree of chemical complexity [Zhang et al. 2017] is promising for future alloy design. Extreme chemical complexity modifies both energy dissipation and defect energy landscapes. Therefore, maximally disordered alloys—as represented by concentrated equiatomic single-phase solid solutions—provide possibilities for alloy design in general, and radiation resistance in particular, that are fundamentally different from conventional approaches for single-element–based alloys. The use of concentrated single-phase alloys has allowed unambiguous interpretation of results based on the energetics of the radiation damage and alloying processes, and the formulation of simple alloying rules to modulate dynamics and control defect production. [Gramberg et al. 2016; Troparevsky et al. 2015; Zhao et al. 2016; Lu et al. 2016] This approach lends itself to the type of predicative capability necessary for design via compositional tools and models and to high-throughput screening of many compositions. [Troparevsky et al. 2015] A basis for designing new radiation-tolerant materials and structures by manipulating compositional complexity (Figure 34) would complement and extend the high-sink-strength approaches discussed earlier. However, a key barrier to implementing such a strategy is that classical potentials are not adequate to deal rigorously with this level of alloy complexity. Consequently, new ways of producing highly accurate potentials for N-component systems (where N>3) are needed, as is the development of scalable ab initio simulation methods that can deal with moderate numbers of atoms (10^3–10^4) to explore defect production and evolution.

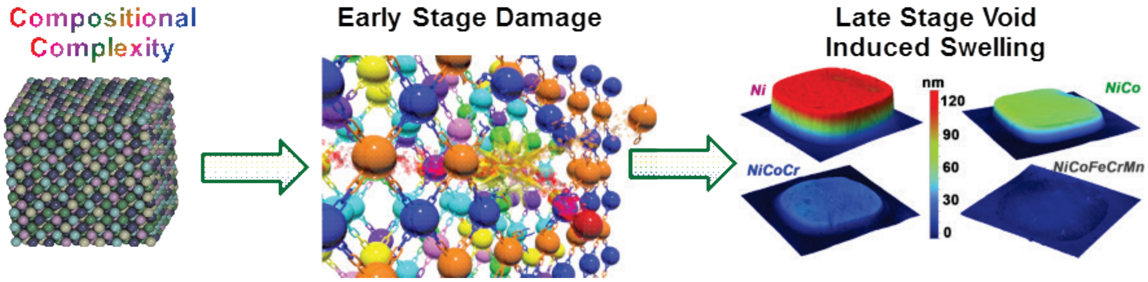


Figure 34. Aspirational approach to a design basis for radiation damage tolerance by understanding and controlling early-stage damage through compositional complexity. | Left and center images courtesy of Oak Ridge National Laboratory. Right image reprinted with permission from Y. Zhang et al. 2017. Atomic-level heterogeneity and defect dynamics in concentrated solid-solution alloys, *Curr. Opin. Solid State Mater. Sci.* 21(5), 221–237. Copyright 2017 American Chemical Society

Optimized microstructures may be created through a combination of micro/nano chemical and microstructural/nanostructural elements. Doing so requires the ability to understand and control the relationship between chemistry and structure. Both theory [Si-Ahmed et al. 1982; Sniegowski et al. 1983; Wolfer and Mansur 1980] and experiment [Allen et al. 2005] have shown that the growth of microstructural features is strongly influenced by changes in chemistry at the surface of the defect. But experiment, theory, and computation have not sufficiently advanced to adequately capture the chemistry–structure interplay at these interfaces (see PRD 3). Thus, the understanding of radiation effects often is limited to small subsets of the microstructure, in isolation from the whole.

Synthesis and processing to create stable, tailored microstructures

The synthesis and processing of advanced reactor materials requires basic research focused on developing reaction pathways and thermomechanical processes via fundamental understanding of new chemistries and associated phase thermodynamics, interfacial dynamics, and the role of deformation. These efforts may benefit from recent and future advances in nanoscale and processing science. [DOE 2007, 2016] Design targets include new final compositions; an understanding of the thermodynamics of new phases, the energetics governing pathways to them, and their long-term stability; the inherent neutronics of these phases; and the use of thermal and deformation processing to achieve the targeted microstructures and associated properties for extreme nuclear energy environments.

Understanding the fundamental chemistry and physics of phase formation, which is often governed by kinetics rather than thermodynamics, will enable the formulation and synthesis of non-predicted phases and new discoveries. For example, gamma irradiation of water enables phase formation driven by solvated electrons in solution; the irradiation dose correlates with the concentration of solvated electrons formed, thereby dictating the reduction routes of the synthesis. [Belloni 2006] Targeted outcomes include (1) controlled reduction of metal ions, (2) well-known rates of reaction, (3) radiation-stable products, and (4) temperature-stabilized phases. Uniform nanoparticles of metals, alloys, or core-shell assemblies are typically desired. Despite not being predicted by equilibrium thermodynamics, AgNi alloy nanoparticles of designed stoichiometries have been synthesized and characterized [Zhang et al. 2009]; and the method has been extended to nuclear fuel compositions (see Figure 35). [Zhang et al. 2010; Nenoff et al. 2011; Nenoff et al. 2013]

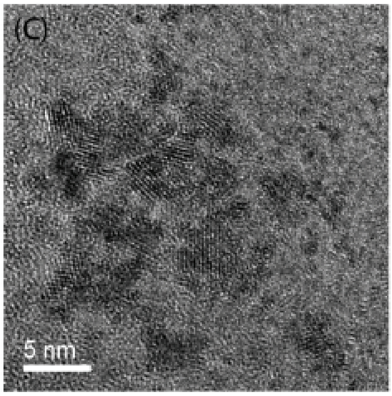


Figure 35. d-UO2 NPs at pH=3, with 7 days irradiation. | Image courtesy of T. M. Nenoff et al. Synthesis and low temperature in situ sintering of uranium oxide nanoparticles, *Chem. Mater.* 2011, 23(3), 5185–5190, copyright 2011 American Chemical Society

Methods targeting metastable phases may hasten discovery. These include the initial synthesis of reactive novel actinide organometallic phases, oxohydroxides, and nanomaterials that are subsequently used as highly reactive reactants. One example is actinide-containing nanoporous metal-organic frameworks. These are a means of synthesizing metastable phases as precursors/reactants to novel condensed phases. [Li et al. 2017] Examples of other pathway targets include a direct pathway for converting UF_6 to fuel and uranyl nanostructures [Qui et al. 2012] that are fully formed as nanoclusters and therefore stable, possibly incorporating self-healing properties.

Once the basic understanding of chemical complexity and of sink design for radiation tolerance is available, predictable and efficient processing routes are needed to incorporate such features into materials at the necessary concentrations. Developing such routes will require an understanding of reaction mechanisms during thermomechanical treatments, including targeted self-healing properties and defect sinks/defect reaction kinetics. It is possible to incorporate desirable features during processing, e.g., via powder metallurgy and heat treatment in nano-oxide dispersion-strengthened steels, [Odette et al. 2008; Miller et al. 2005; Ukai et al. 2002; Klueh et al. 2005] or via severe plastic deformation, as in Cu-Nb nanolaminates produced by accumulative roll bonding. [Chee et al. 2010] Alternatively, one could rely on the ability of materials to self-organize during irradiation, such as in a high density of nanoprecipitates. [Demkowicz et al. 2010; Chee et al. 2010] The resulting nanofeatures may be stable under irradiation, in contrast to the metastablility created in them during fabrication. For solid fuels, basic research supporting the design and development of advanced chemical techniques and methods is needed for processing materials with tailored sink strength and porosity.

Additive manufacturing (AM) (also known as layer-by-layer deposition, direct digital manufacturing, and 3D printing) has grown explosively as an industrial materials processing route to more efficient use of starting materials (versus subtractive manufacturing processes) and to building tailored, sometimes intricate, structures from 3D models using compositions controlled by the feedstocks. [Frazier 2014; Pietryzk 2015] As in other processing schemes, an understanding of thermodynamics; reaction kinetics; matter and heat transport; thermal gradients; and associated deformation, chemical reaction, or solidification phenomena are keys to AM process development and control to achieve the desired structure and properties. Conventional materials produced by AM can often be considered new materials with unique properties. The ability to spatially vary and control microstructural features or composition using AM techniques allows for all-encompassing material, component, and system design, avoiding the limitations of conventional manufacturing. Application of AM to nuclear energy is in its infancy, but an example of progress in this area is using metal AM to produced integrated fuel plates for the High Flux Isotope Reactor at Oak Ridge National Laboratory. [Hehr et al. 2017] From a basic science viewpoint, however, the greatest value of AM may be (1) for fabricating innovative specimens and experimental platforms to efficiently explore and discover phenomena related to extreme environments, and specifically (2) for exploring fundamental issues related to enabling materials design, processing, and/or high-throughput screening of materials (as discussed later in this section) predicted to be stable under extremes.

Development of accurate predictive methods and models

The reactor environment presents the challenge of predicting key materials properties such as stability, durability, aging, fission gas production, decay species interactions, and corrosion. Developing accurate predictive methods to build "surety" into all facets of advanced nuclear reactors (including structural materials and nuclear fuels) is essential, but the difficulty in predicting materials behavior in extreme environments is a major challenge to developing better materials design approaches. However, the problem lends itself to high-performance computing, which allows the modeling and prediction of new structural materials and fuels and/or of events such as metal-gas interactions, defect growth, and the formation and evolution of nanoscale structures that serve as bases for design rules. Current advances in ab initio molecular dynamics simulations—combining traditional molecular dynamics with electronic structure methods that use density functional theory (DFT) electronic optimizations at each time step [Parkes et al. 2016]—will allow the inclusion of temperature effects. This will improve the ability to design novel fuel and structural materials (and their surface chemistry interactions) based on predicted behavior at realistic temperatures.

Advanced efforts in f-electron element electronic structure modeling, combined with dynamic thermal and neutronic effects, are essential for the breakthrough design of new solid fuels. Simultaneously, model development and testing on high-performance computing resources is necessary. These tools will allow for fundamental code development that addresses the multitude of permutations of the radiological environment relatively rapidly and will accelerate the discovery and design of new fuels.

Despite many years of effort, in many cases, accurate atomic potentials are still not available for compositions associated with nuclear materials, even in the unirradiated condition. Improved potentials must be validated by DFT and potentially more accurate treatments and more rigorous approaches such as quantum Monte Carlo. [Martin et al. 2016] (These potentials will include far-from-equilibrium conditions (e.g., when atoms are very close, as occurs in radiation damage or near high-energy transition states) and potentials for chemically complex, multicomponent systems.) The validations must fully consider relativistic effects to lower this barrier to materials design. New approaches focused on an automated evaluation of a landscape of parameters to generate optimal potentials would help accelerate discovery and design. Additionally, testing of developed potentials for application in extreme environments will require a substantial body of critical experimental data for properties at those conditions—much of which is missing, challenging to obtain at the atomistic level, and typically not sought.

The ability to model materials behavior over many length scales is a current challenge for many systems that are less complex than those that operate at the extremes of the nuclear reactor environment (see PRD 4). However, progress in this area is essential for advanced design approaches because property targets and material/component lifetimes serve as the desired outcomes. The degradation front moves though materials, creating both time and spatial distributions of damage. The relationships among nanoscale atomic interactions of atoms, bonds, and neutronics need to be correlated with the mesoscale damage front movement through structural and actinide-bearing materials to accelerate the design process. The ability to relate phase field modeling to known compositions and structures that accurately reflect radiation damage and other degradation modes, and then apply that model to advanced compositions and phases, is a necessary predictive capability for materials design.

High-throughput screening

High-throughput computational screening is an important part of accelerated computational design and synthesis/processing of both functional and structural materials. [Curtarolo 2013] Therefore, there is a need for basic scientific research and complementary tools and techniques that validate high-throughput screening of new theories, atomic potentials, models, and analysis frameworks for the structural materials and solid fuels needed for future nuclear energy systems—including those necessary for materials design. In addition, effective relevant schemes are needed for high-throughput experimental data generation for nuclear materials. One particularly promising approach for radiation-tolerant materials design, as well as discovery, is the use of thin films to screen for the inherent sink strength of various interface configurations and compositions. With design considerations and targets in mind, high-throughput experimental methods for screening thermal stability, cracking, corrosion susceptibility, and so on are ripe for development. These will include possible uses of AM. Rigorous ways of generating appropriate data computationally for structural materials and nuclear fuels also should be explored. Such advances can significantly reduce the time required to develop next-generation nuclear materials.

As high-throughput experimental and computational data are generated, advanced data analysis tools and machine learning techniques must be applied to fully use and digest the information in these data sets. Such tools could also be applied to the extensive existing databases for current materials to unearth trends heretofore unrecognized. Use of these advanced analytical and learning tools may not only validate existing models used in computational materials design; they may also lead to unanticipated results and the discovery of new materials and improved modeling and simulation approaches resulting in even better design rules for structural materials and solid fuels.

Physically based models to guide and accelerate materials design and discovery through experiments and integration with theory and modeling

Advances in understanding of the basic physics and chemistry of structural and nuclear fuel materials (surrogate and actinide-containing)—from atomic behavior through molecular to bulk material properties—is necessary for their eventual use in environments containing high radiation fields, high temperatures, reactive species, and the production and decay of fission products. For materials design, the experimental and theoretical work to foster this understanding needs to inform predictive models that uniquely relate composition and associated microstructures to the properties and performance relevant to the characteristic extreme conditions of nuclear systems. Developing the underlying science for these models will enable the efficient design of structural materials and solid fuels based on the absorption and scattering of neutrons, the presence of other fission products, gamma radiation, self-decay, and the effects of deformation and high-temperature environments.

Further experimentation with ion irradiation is needed to understand and model damage and synergistic effects in reactor materials (that is, in a neutron environment) and to accelerate dose accumulation to examine long-term behavior. However, rigorous methods to convert analytical results from ion beam experiments to equivalent damage under neutron irradiation are generally lacking. Better approaches to translating results from ion beam irradiation into equivalent neutron doses and dose rates will result in a much larger database. It can be used to develop better models for predicting the extent of damage and its effects on material properties, as functions of composition and structure, to aid the design of new materials. When this challenge is met, such approaches can also be used for accelerated testing and validation of design rules.

Experimental research is key for (1) validating and informing future models for materials design and (2) observing processes that are not currently captured by any models. The latter will include the discovery of rare or unexpected events and stochastic processes (see PRD 5) that may lead to entirely new approaches to the design of structural materials and solid fuels. Although doing so is highly challenging, measurements must be made at the right precision and scale to validate these models for design. The physics that drive experimentally accessible intrinsic length and time scales are increasingly accessible via atomistic-level first-principles electronic structure and molecular dynamics models. A set of models exists at even smaller length scales that experimental techniques still cannot probe. Enhanced diffraction techniques in high momentum transfer ranges are necessary to enable accurate pair distribution function analysis, or new revolutionary techniques that are able to probe accurately at extremely small length scales. Such progress can lead to transformational atomic-scale discovery and design rules for new nuclear materials.

Material design approaches would also benefit from feedback from refined or re-imagined experimental methods at longer length scales to better characterize materials in real applicable radiation and high-heat-flux conditions. New in situ and correlative techniques are needed that access extreme environments and explore synergistic effects and their implications for materials design. Of particular interest in this area is the potentially immense value of in situ characterization to research on predictable synthesis routes and processing for modified and new structural materials and fuel forms. One example is the formation of lanthanide nanostructures with simultaneous imaging using a microfluidic stage in a transmission electron microscope. [Nenoff et al. 2012] The nanostructures that formed were directly correlated with the electron dose of the beam (see Figure 36). Basic nuclear materials research that can benefit from this capability includes studies of fuel materials, such as uranium carbides or nitrides that are sensitive to oxidation, and structural alloys with novel nanoscale additives processed in various ways. Another example is the use of neutron scattering to capture stress development during friction stir weld processing of an alloy. [Woo et al. 2017]

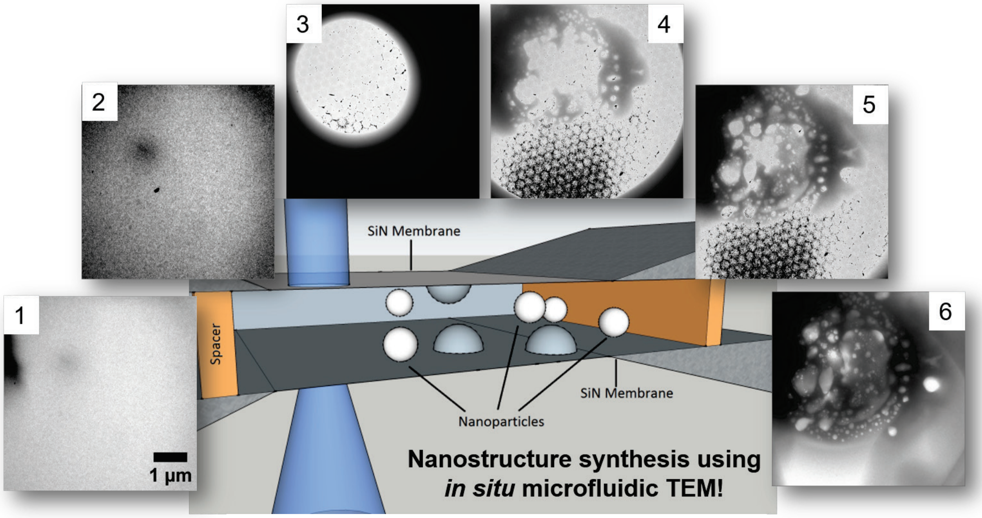


Figure 36. $Y(NO_3)_3 \cdot 4H_2O$ solution. (1) initial nanostructure nucleated by focusing the electron beam, (2) the electron beam focused to a point on the nanoparticle in solution, (3) microstructure formation, (4) continued microstructure growth, (5) and (6) final microstructure resulting from the focused electron beam, with possible cavity growth. All images are at the same magnification. (Background honeycomb pattern is saturation of camera due to focusing the electron beam.) | Images courtesy of Sandia National Laboratories

Panel: Crosscutting Themes

During the workshop on Basic Research Needs for Future Nuclear Energy, all four panels pointed to the need to understand the fundamental chemical and physical processes that occur under extreme conditions, in order to enable the development of future reactor concepts. The processes that occur in structural materials, coolants, and fuels must be understood across broad spatial and temporal scales—from atomic to macroscopic length scales and from femtoseconds to years. These requirements, which were common to all four panels, cannot be met with today's analytical and computational tools. New approaches are needed that take advantage of in situ measurements—including multiple simultaneous measurements that can probe both chemical reactions and structural changes—to provide a more complete view of the multitude of impacts that occur in the extreme coupled conditions to which these materials are exposed. Importantly, it was underscored that experimental methods need to be closely integrated with computational tools to not only predict and simulate degradation processes but also enhance and accelerate the interpretation of experimental data. This integration requires advancing the scalability of computational approaches so as to model realistic systems, as well as effecting new methods that leverage increasing experimental knowledge about the energy surfaces that dictate system behavior at different length scales. New data analysis approaches are needed to interpret and assimilate heterogeneous data from vastly different experimental and computational methods, and to accelerate initial data interpretation to optimize experiments—especially those conducted at major facilities where access time is at a premium. The development and integration of these experimental and computational methods will expedite the rapid advancement of future nuclear energy systems by supporting the essential need to understand and predict chemical and physical changes to materials, coolants, and fuels.

Current Status and Recent Advances

New approaches are being developed to rapidly assess the response of relevant materials through in situ and operando studies. Integration of multiple characterization tools will allow simultaneous monitoring of various processes. It is critically important to closely couple theory with experiment, to predict and confirm experiments and to bridge gaps across time and length scales to fully understand future nuclear energy systems. Next-generation algorithms will be required that span from ab initio density functional theory calculations to continuum models that capture the complexity of liquid/solid and solid/solid interface interactions, and that are applicable to the complex alloy compositions envisioned for application. New methods assimilating information from multiple experimental and computational studies that represent different length and time scales or dimensionality are being developed, as are advances in data analytic methods.

Recently developed techniques and expanded capabilities at national neutron and x-ray synchrotron facilities provide unprecedented opportunities to probe interactions and reactions in real time, at temperature, and in realistic chemical environments. These capabilities—including spectroscopy, scattering, and imaging techniques—have been employed to study materials in situ and operando. These explorations include imaging of structural materials and even systems of components, local structure determination, examination of interfaces, and investigations of chemical dynamics. Liquid and molten salt structures can be determined at high temperatures in both irradiated and unirradiated conditions. These capabilities are just now starting to provide new insights into the structure-process-property relationship in fuel, coolant, and structural materials.

X-ray, neutron, and electron microscopy imaging technologies have made tremendous advances in recent years, including improvements in resolution and sensitivity and the capability to investigate in situ and operando conditions. For example, recent advances in the resolution of spatially resolved neutron detectors allow the use of neutron resonance absorption imaging to characterize fuel elements in the

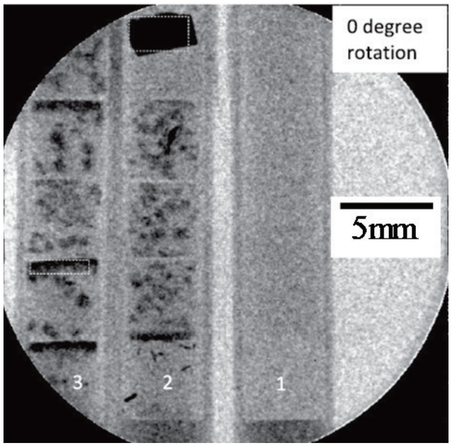


Figure 37. Nuclear resonance contrast tomographic imaging of UO_2 pellet assemblies containing tungsten particles (dark regions). Assembly 1: densities of Urania varying from 48 to 96% of theoretical density. Assembly 2: tungsten inclusions introduced with 75–200 μm wires and particles. Assembly 3: PMMA (plastic) inclusions used to introduce voids during pellet sintering, as well as tungsten inclusions similar to those in assembly 2. | Reprinted from *Nuc. Mater.* 440(1–3), A. S. Tremsin et al., Non-destructive studies of fuel pellets by neutron resonance absorption radiography and thermal neutron radiography, 633–646, copyright 2013, with permission from Elsevier

cladding. Figure 37 shows neutron contrast tomographic imaging of UO_2 pellet assemblies containing tungsten rods and particles of different dimensions. [Tremsin et al. 2013] The densities of the two materials are high and similar, and conventional absorption contrast imaging is insensitive to the difference. However, in the resonance-based image, tungsten rods and particles are readily identified as the dark regions. The same approach can be used to image isotopic distributions, such as ^{235}U particles in a ^{238}U matrix, to reveal heterogeneity in the distribution.

Advances in aberration–corrected transmission electron microscopes hold the promise of incorporating in situ tools with the objective lens while retaining high resolution capabilities. In Figure 38, an Ni_3Al sample is exposed to oxygen in situ at high resolution so the atomic mechanisms of ledge growth of the oxide can be directly observed. The two images show the same sample initially and 40.5 seconds after introducing oxygen into the system. They demonstrate the value of evolutionary measurements of a single sample, enabled by nondestructive techniques that make growth of oxide layers apparent.

Scanning transmission electron microscopy (STEM) instrumentation now provides high-atomic-scale imaging with equally high-spatial-resolution spectroscopy, providing column-by-column chemically sensitive atomic-scale imaging. For example, using K_α emission lines, element-specific distributions of zirconium and yttrium at a grain boundary in yttria-stabilized zirconia were obtained with aberration-corrected STEM (Figure 39). [Feng et al. 2016] The bottom panels show element-specific line profiles that clearly reveal the heterogeneous distribution of zirconium across and along the grain boundary. Similar advances in electron microscopy enable researchers to decipher local valence, oxidation state, and varied aspects of the electronic structure of buried internal interfaces. Importantly, new capabilities have been developed for studying samples in more realistic environments using electron microscopy, although further advances are needed to observe the full range of materials required for applications to nuclear systems.

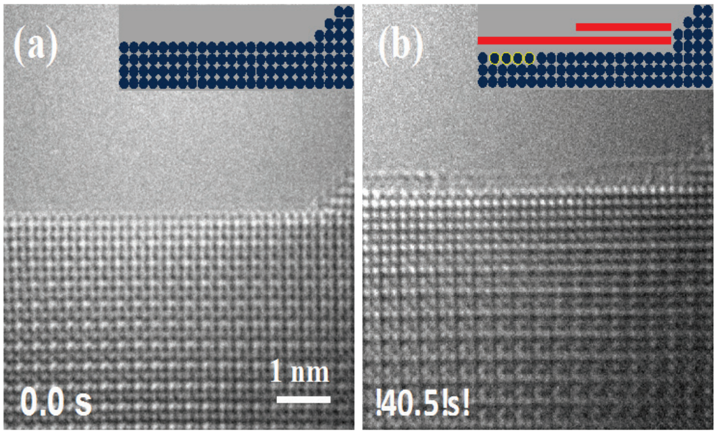


Figure 38. In-situ observation of oxide growth on Ni_3Al imaged at high resolution in an aberration-corrected transmission electron microscope. | Image courtesy of Guangwen Zhou, SUNY Binghamton

Complementary simulation of these heavy-element–bearing nuclear materials remains a significant challenge, as electronic structure methods must include relativistic effects, both scalar and spin-orbit splitting. [Wilson 1988; Dolg 2015] Rigorous four-component solutions are available [Visscher et al. 1994] but are typically intractable except for benchmarking of quite simple systems. To enable codes to take advantage of modern supercomputer architectures, such as the next-generation supercomputer Summit, the Oak Ridge Leadership Computing Facility (a DOE Office of Science user facility) has chosen the DIRAC code as 1 of the 13 partnership projects in its Center for Accelerated Application Readiness program. [Visscher et al. 2017] DIRAC builds on earlier work on the parallelization of MOLFDIR. [Pernpointer et al. 2000]

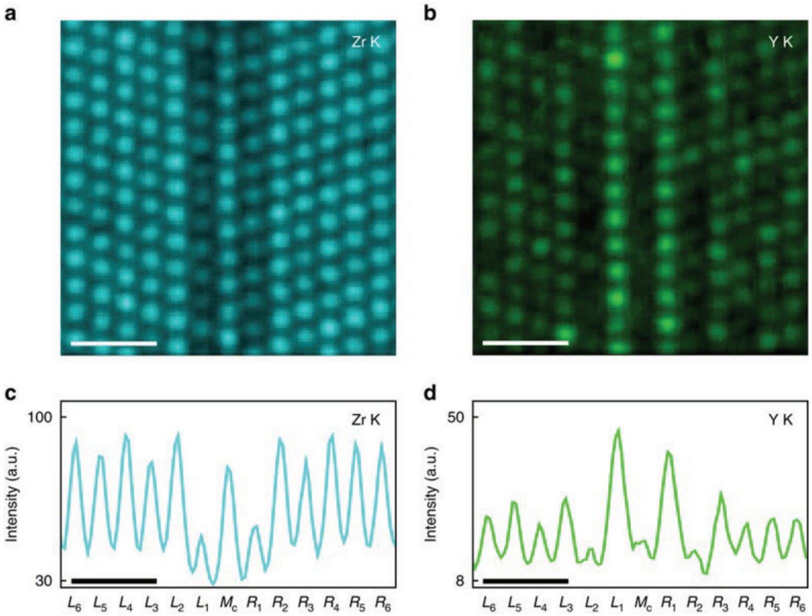


Figure 39. Abberation-corrected STEM energy-dispersive x-ray spectroscopy elemental maps for (a) zirconium and (b) yttria at a grain boundary in yttria-stabilized zirconia. Kα emission intensity profiles for (c**)** zirconium and (d) yttria. Different scales are used for the two intensity profiles. Scale bar is 1 nm. | Image courtesy of B. Feng et al. 2016. Atomically ordered solute segregation behaviour in an oxide grain boundary, *Nat. Commun*. 7, 11079.

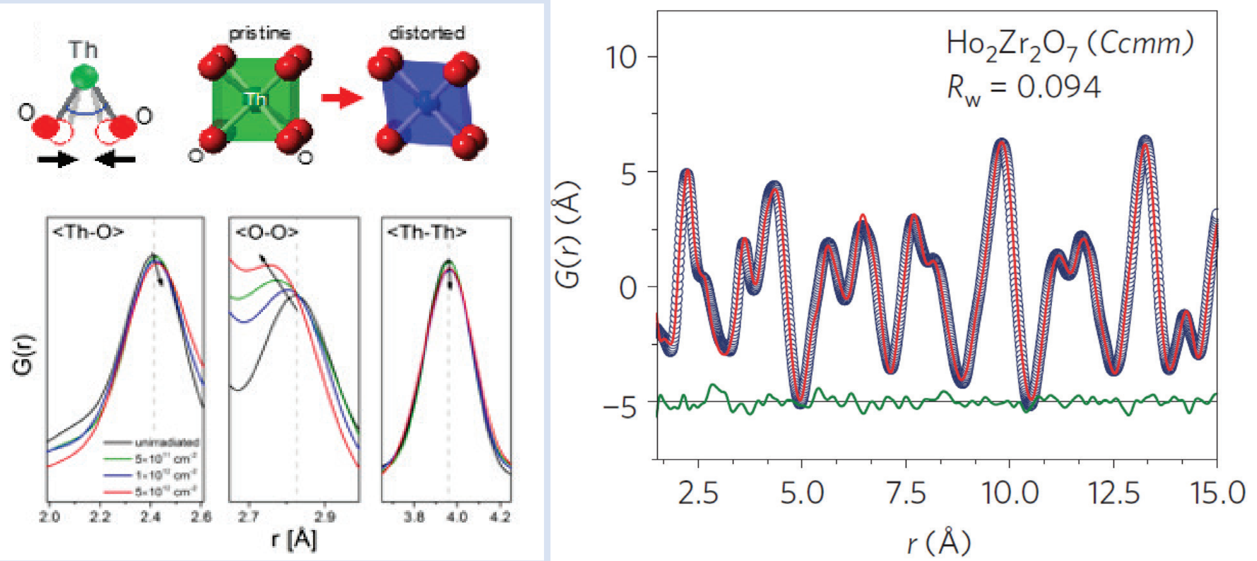
The limitations in the reliability of computed energetic and materials properties become particularly important in light of the importance of atomic-level defects and their role in the cascade of events that eventually result in material failure. For example, localized inhomogeneities, such as ultra-small quantities of a deleterious solute at grain boundaries, may have an outsize influence on the local brittleness. Innovative approaches are needed to isolate that "needle in the haystack" through spatio-spectroscopic approaches combined with computation that can isolate and identify chemical perturbations and their unique signatures. There is a need for new potentials to extend simulation capability beyond metals that contain more than two or three elements, and for protocols that allow input from one simulation method to be passed to the next-higher length scale method.

Perhaps the greatest opportunity—and the most significant challenge—is to combine characterization techniques, computation, and data analytics to fully interrogate the data and to use insights from one approach to inform the interpretation of results from the others. There are opportunities to rapidly explore materials space to evaluate, in silico, new compositions, properties, and performance. Such approaches have seen success in areas outside the nuclear field and have resulted in reduced times for alloy development and deployment and for assessing the performance of components in service. Furthermore—with enhancements in computer architecture, the advent of exascale computing, the application of machine learning methods to materials discovery, and developments in instrumentation that narrow the spatial and temporal differences between simulation and experiment—the time is opportune to work at the intersection of experimental capabilities, simulation, and data analytics.

As an example of the advantages of combining different methods consider how the structure of molten $ZnCl_2$ was elucidated using a combination of neutron diffraction, Raman spectroscopy, and simulation. Ab initio molecular dynamics (AIMD) was used to model the structure of $ZnCl_2$ at 327°C. The structure factors and pair distribution functions derived from AIMD matched well with those measured previously by neutron diffraction. Raman spectroscopy was also used to investigate the structure of liquid $ZnCl_2$. This information was directly compared with the results of MD simulations, enabling direct testing of the simulation and refinement of training sets. [Alsayoud 2016]. Although the experimental studies were done separately, it is possible that techniques could be combined within a single experiment to allow changes in structure at a surface to be compared with chemical changes in the interfacial fluid (see the sidebar “Advanced Materials Characterization: Neutron Total Scattering Experiments”). This study also demonstrated the power of closely coupling experimental measurement with simulation to obtain more detailed understanding of the resulting structures. In this context, advances in scaling to enable longer AIMD simulation time scales and on-the fly analysis of a simulation could ensure either that simulated systems are at equilibrium, or that enough statistics have been gathered to yield predictive insight.

Advanced Materials Characterization: Neutron Total Scattering Experiments

Neutron scattering techniques like those available at the Spallation Neutron Source DOE user facility provide unique capabilities for studying nuclear materials. For example, neutron pair distribution function (PDF) can provide diffuse scattering contributions that are omitted in traditional diffraction experiments. PDF can provide unique structural insight into local aperiodic defect configurations, as well as disordered and amorphous domains. Each peak in a PDF represents a specific atom-atom correlation; the position corresponds to the pair spacing distance, and the area under the curve is related to the coordination number. Further, neutrons scatter strongly from low-Z elements, permitting detailed analysis of both cation and anion defect behavior. The image at left shows an example of how neutron PDF was applied to characterize local structural evolution and irradiation-induced defects as a function of irradiation fluence in irradiated thoria. [Palomares et al. 2017] The defects in ThO_2 result in a change in the mean O–Th–O bond angle and a distortion of the local ThO_8 polyhedra. Neutron PDF can also be used to assess the local order in disordered complex oxides, as shown in the image at right. Disordered $Ho_2Zr_2O_7$ pyrochlore with a long-range defect-fluorite structure consists of short-range orthorhombic distortions, which result in a higher degree of local order than previously was thought. [Shamblin et al. 2016]



Neutron scattering results for irradiated thoria and disordered complex oxides. | Top left: image courtesy of R. Palomares, University of Tennessee–Knoxville. Bottom left: R. I. Palomares et al., Defect accumulation in swift heavy ion-irradiated CeO_2 and ThO_2, *J. Mater. Chem. A* 5, 12193–12201 (2017). Right: Reprinted by permission from Nature Publishing Group. *Nat. Mater.*, Probing disorder in isometric pyrochlore and related complex oxides, J. Shamblin et al., copyright 2016.

High-fidelity, high-performance computing is becoming more predictive for certain physical properties and processes that are relevant to nuclear fuels as well. For example, recent studies have extensively investigated the diffusion mechanisms of xenon through density functional theory and atomistic modeling. [Andersson et al. 2015] Figure 40 provides a demonstration of the good agreement of MD simulations of displacement cascade–induced diffusion of U, O, Kr, and Xe with experimental data indicating a regime of temperature-independent diffusion in nuclear fuel. These simulations [Cooper et al. 2016] used recently developed interatomic potentials and modeled the diffusion of both the host U and O on the fluorite UO_2 lattice, along with the fission gases Kr or Xe at a local concentration of 1%. Figure 40a shows snapshots of the evolution of a 75 keV displacement cascade at 327°C in which the U and O atoms are represented by semi-transparent spheres. Their color indicates the local temperature (red = hot and blue = cold). Displaced Xe atoms are represented by opaque spheres; their color indicates the displacement relative to the initial configuration (red indicates displacement greater than 0.5 nm).

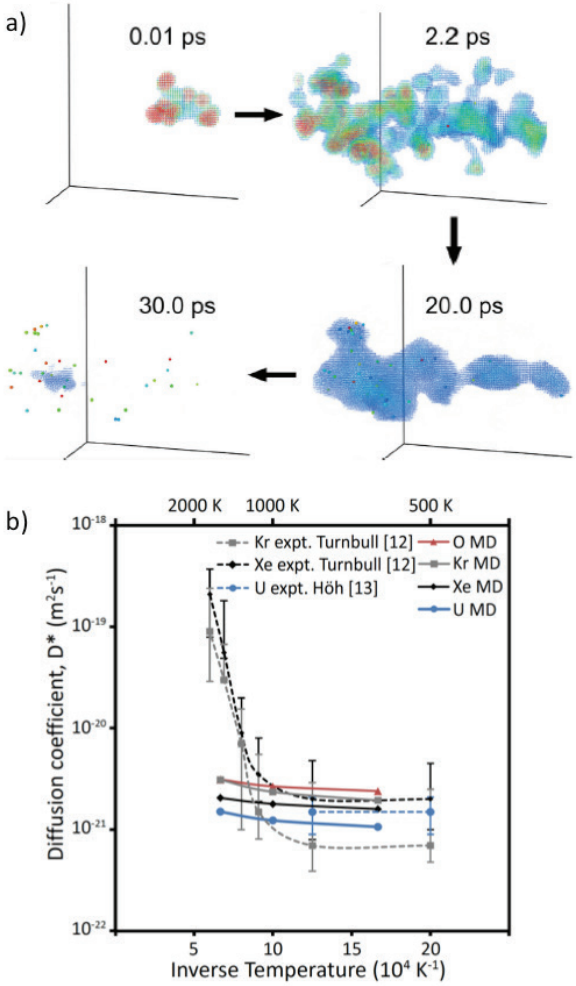


Figure 40. Atomistic modeling of radiation effects in materials are rapidly becoming more predictive. (a) Visualization of defects created by 75 keV displacement cascade evolution in UO_2 containing 1% xenon (top panel); the darker colored spheres indicate xenon atoms displaced from their original positions. (b) Resulting diffusion coefficient of U, O, Xe, and Kr calculated by molecular dynamics (solid lines) and compared with available experimental data (dashed lines). | Reprinted from *J. Nucl. Mater.* 481, M.W.D. Cooper et al., Simulation of radiation driven fission gas diffusion in UO_2, ThO_2 and PuO_2, 125–133, copyright 2016, with permission from Elsevier

These examples illustrate the significant opportunities that exist for atomistic modeling of actinide-bearing materials (both solids and liquids) at realistic simulation conditions. Such simulations are also vital in their capacity to inform higher-scale coarse-grained finite element and even phase field simulation methodologies. Recent work has illustrated the ability of modeling to advance the fundamental understanding of radiation-induced microstructural evolution. An impressive ability to capture the multiscale nature of radiation effects on body-centered-cubic structural materials has recently been articulated, at least in terms of the evolution of the interstitial defect clusters and sub-visible vacancy cluster distribution in neutron-irradiated iron. [Wirth et al. 2015] Radiation-induced precipitation in both steels and binary alloys has also been successfully studied using atomistically informed phase field models. [He et al. 2017]

Opportunities exist to combine in situ irradiation experiments with modeling, to examine the fine details of defect evolution under continuous irradiation, and to verify fundamental assumptions/uncertainties with respect to damage production and the kinetics/energetics of irradiation defects. For example, there is a need for additional, high-fidelity experimental characterization of the defect cluster microstructure in irradiated materials at irradiation temperatures covering the range over which interstitial and vacancy point defects migrate, annihilate, and cluster. This will help to validate the defect cluster diffusion kinetics and reaction rate constants that are inherent to the reaction-diffusion cluster dynamics. Kinetic Monte Carlo modeling approaches also are needed. Future modeling and experimental studies are also needed to further understanding of the interactions among defect clusters and their interactions with extended microstructural sinks. For example, there remain numerous unresolved questions about defect cluster evolution as the result of cascade overlap. And questions remain regarding the quantitative details of how to treat the reaction rates between defect clusters and various microstructural sinks—including dislocations, grain boundaries, nanometer-size precipitate interfaces—as well as reactions among the defect clusters themselves. Finally, the radiation defect evolution modeling results have focused almost entirely on the evolution of vacancy- and interstitial-type defect clusters in irradiated materials, without any consideration of the coupling of the defect and solute/impurity fluxes. There is longstanding literature on radiation-induced segregation in austenitic alloys, as well as more recent work on radiation-induced segregation in ferritic-martensitic materials. The coupling of the defect and solute fluxes that occur under irradiation to thermodynamic predictions of radiation-induced phase formation is receiving increasing attention. Seamless integration of evolving defect physics with radiation-induced segregation and changes in second-phase precipitates represents a true grand challenge within the radiation effects community.

Rapid materials discovery for use in future nuclear energy systems could be expedited by coupling high-throughput experiments and computations. Generation of large datasets coupled with advanced data analytics could help define design rules for a new generation of materials. To date, novel high-throughput methods have been developed for parallel structure-property. One example is a testing rig that can accommodate multiple specimens (in this case, produced by additive manufacturing) subjected to load, environment, and radiation fluxes together with in situ diagnostics [Bruemmer et al. 2014]. Other combinatorial approaches for synthesis and rapid screening for properties such as phase equilibria, radiation tolerance, and susceptibility to specific degradation methods are also still nascent.

Analogous computational screening of materials aligned in the vein of the Materials Genome Initiative has advanced tremendously in other energy conversion sectors that benefit from calculations of thermodynamic quantities. [Curtarolo et al. 2013] Nevertheless, the evolving and nonequilibrium nature of materials in reactor conditions demands progression beyond the current state of the art. New approaches need to incorporate

1. Multiple stimuli (radiation, stress, corrosion, temperature)
2. New methods for high-throughput computation of kinetic parameters (e.g., diffusion) that enable the inference of likely, and potentially unconventional, kinetic pathways from knowledge of energy landscapes and transition rates
3. Finite temperature phase equilibria, including the possible effects of anharmonicity

A truly integrated and closed loop with high-throughput experiments will advance materials understanding and design and is on the horizon.

Science Challenges and Opportunities:

The extreme conditions in a nuclear reactor represent significant challenges to the structure and chemical stability of the component materials—the fuels, coolants, and structural materials. The following representative challenges identified in the workshop panels highlight the hierarchical and multiple length and time scales at which damage can occur, and how the presence of a multitude of interfaces and phase boundaries can lead to unanticipated behavior that is difficult to predict or even characterize at the current state of the art. The motivation and opportunities for advanced characterization, computational, and analysis methods is demonstrated.

Microstructural control of oxidation response

The performance of a metallic component exposed to high temperatures in a water-, sodium-, lead-, or gas-cooled reactor is susceptible to degradation and associated metal loss from oxidation. An ideal material would quickly form a thin, impenetrable, stable oxide. Real materials form complex oxides that may lead to spallation and reinitiation of fresh oxidation, or they may form local pitting or cracking sites.

As an example, three different oxides can form on the single-metal surface of the nickel-based Alloy 625 after exposure to supercritical water (Figure 41). [Xu et al. 2012] This complexity is believed to be controlled by the different types of crystallographic organization on the surface, whereon a “flat” oxide forms on a surface having a <111> grain, while a “rough” oxide forms on the non–<111> surfaces. The boundary shown is a high-angle boundary intersecting the surface, leading to a flaky oxide that differs from that formed on bulk grains. Thus, the nature of the oxide formed is dependent on the grain orientation and may be sensitive to the boundary type too. This richness in oxidation behavior (i.e., different oxides form simultaneously, and the macroscopically formed oxide is a composite of distinct oxides) leads to the possibility that the overall oxide can be designed through thoughtful combinations of individual grain and grain boundary building blocks. Making use of a design platform based upon microstructural organization, and enhancing corrosion resistance, require

- a far better understanding of the atomic structure and composition of the native oxide as a function of grain orientation
- a molecular-level understanding of the interaction of the coolant with the native oxide and of how these processes are modified as impurities are introduced into the coolant
- an understanding of the combined kinetic and thermodynamic pathways that lead to oxide formation in individual microstructural building blocks and at interfaces
- the ability to control the synthesis of the desired of microstructural building blocks at interfaces

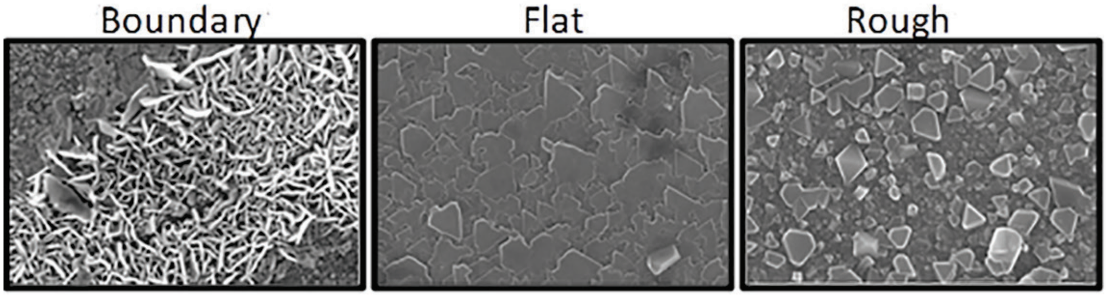


Figure 41. The corrosion morphology changes depending on the surface orientation to the environment or the grain boundary orientation. Systematic design of the overall material structure could better control the stability of the overall oxide, thus extending component lifetime. | Image courtesy of Todd Allen, University of Wisconsin–Madison

Toward those ends, one approach is to develop novel methods to rapidly capture large data sets from oxidation experiments and computations and use machine learning approaches to generate knowledge and predict and optimize microstructural design strategies.

Local compositional changes induced by irradiation and temperature

Irradiation at elevated temperatures induces numerous changes in the microstructure and local composition. For example, irradiation produces 2D and 3D defects, e.g., dislocation loops, stacking fault tetrahedra, and voids. It also induces compositional modifications associated with the diffusion of point defects, which result in changes in the composition of the grain boundaries as well as segregation of elements to and from the irradiation-induced defects. For example, it has been shown that in face-centered-cubic equimolar alloys such as NiCoFeCrMn and NiCoFeCrMnPd, elemental segregation occurs at loops produced by ion irradiation at 500ºC and by high-energy electron irradiation at 400°C (Figure 42). The segregation of elements to an interface may also have a beneficial impact. For example, stabilization of nanograined metallic structures is possible through control of the composition of the grain boundary. This may indicate possible strategies to design new alloy systems for radiation environments.

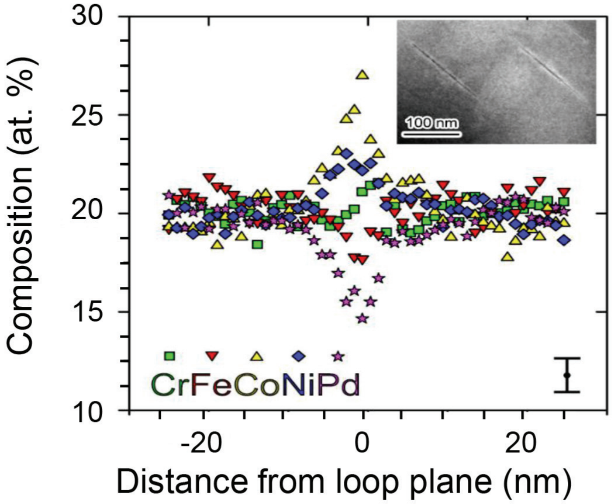


Figure 42. Compositional modification at an interstitial loop produced in NiCoFeCrMnPd equi-molar alloy following 1250 keV electron irradiation at 400°C. Iron and palladium are deficient and cobalt and nickel are enhanced at the loop. | Reprinted from *Acta Mater*, 126, M.-R. He et al., Mechanisms of radiation-induced segregation in CrFeCoNi-based single-phase concentrated solid solution alloys, 182–193, copyright 2017, with permission from Elsevier

The fundamental mechanisms governing elemental segregation need to be discovered in the emerging alloy systems that will be used in advanced reactor systems. The influence of compositional changes at defect sinks on damage evolution under prolonged irradiation at high temperature needs to be understood. Similarly, the role of irradiation-induced compositional and structural changes at interfaces, along with the effects of stresses and temperature on corrosion and liquid metal embrittlement, need to be uncovered.

Degradation driven by coupled phenomena

Materials in reactor systems are subjected simultaneously to external variables that can act independently or synergistically to degrade the properties of the material systems used in nuclear reactors. The external variables include radiation, applied or residual stress, temperature, and corrosive environments due to the coolant and fuel. Some degradation mechanisms—e.g. irradiation-assisted stress corrosion cracking—appear to occur only as the results of simultaneous response to irradiation, temperature, stress, and corrosive environment. The absence of any of those variables can, remarkably, preclude crack initiation. Although the degradation mechanism is known from an engineering viewpoint, there remains a lack of understanding of the physical and chemical processes, and the interplay between them, that ultimately are responsible for crack initiation and propagation. For example, recent progress in understanding liquid metal embrittlement along grain boundaries suggests that a simple reduction in the interfacial energy due to the embrittling species may by itself be insufficient, and that structural unit changes in the interface and plastic deformation processes may contribute to cracking. Similarly, in irradiation-assisted stress corrosion cracking, it is understood that deformation processes at grain boundaries are necessary to rupture the protective native oxide; but the variation in the susceptibility of specific grain boundary locations is not understood.

There remains a need to uncover the fundamental physical and chemical processes that occur at the atomic level, and to link them through the mesoscale to understand the factors that ultimately control the degradation response. That is, the physical and chemical processes that govern the window of susceptibility to degradation need not only to be defined for the operation conditions but also to be understood at a fundamental level. Doing so will require integrating multiple analytical tools within a single experiment to probe the compositional and structural changes simultaneously at appropriate spatial and temporal resolution. The experimental approaches must be coupled with computational methods that allow for comprehensive interrogation of the data.

Understanding chemistry and structures at interfaces

Understanding chemical and structural changes at interfaces is critical to the development of new coolants and materials for future nuclear energy systems. Analytical techniques have improved significantly. It is now possible to determine atomic-scale structure and chemistry in interfacial regions at sub-angstrom resolution with in situ and operando x-ray, neutron, and even microscopy techniques. As an example, the layering of nonaqueous room-temperature ionic liquid electrolytes at a potential controlled electrode/electrolyte interface can be observed directly using x-ray reflectivity (XR in Figure 43). [Zhou et al. 2012] These interface-sensitive methods thus have the potential to help determine the reaction products of corrosion in nuclear materials. By direct comparison with MD simulations, as shown in Figure 43, they also allow validation of simulations and the potentials used in the simulations. However, the use of other spectroscopic and microscopic probes, in conjunction with reflectometry measurements, are needed to examine additional molecular changes in liquids at the interface. In addition, in situ irradiation techniques, such as high-energy electrons, ions, or neutrons, could be used to simulate radiation damage in these studies.

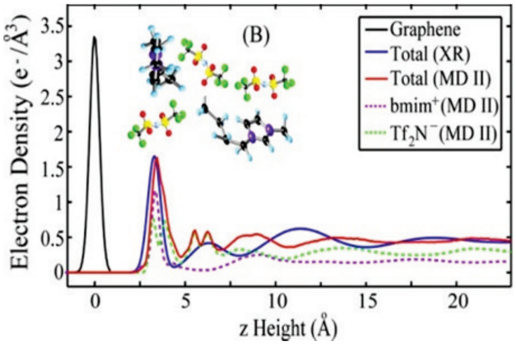


Figure 43. The molecular-scale vertical distribution of room-temperature ionic liquid ions at a graphene electrode under potential control obtained by x-ray reflectivity is compared directly with molecular dynamics simulations. | Reprinted with permission from H. Zhou et al. Nanoscale perturbations of room temperature ionic liquid structure at charged and uncharged interfaces," *ACS Nano*. 6, 9812–9827, copyright 2012 American Chemical Society

Conclusion

The Crosscut panel identified a range of recent advances in characterization and computational capabilities that are highly relevant to understanding the fundamental chemical and physical processes that occur under extreme conditions in order to enable the development of future reactor concepts. However, current capabilities will not be sufficient to elucidate chemical and physical processes that occur over broad spatial and temporal scales—from atomic to macroscopic length scales and from femtoseconds to years. New in situ and multidimensional characterization tools are needed to probe both chemical reactions and structural changes simultaneously. These experimental techniques must be closely coupled with emerging data analysis tools to assimilate and interpret large amounts of data, providing unprecedented information on the highly coupled processes that occur under extreme environments. Advances in computational tools are needed to advance the scalability of computational approaches to yield realistic systems models. Together, these new capabilities provide the underpinning knowledge required to understand and predict chemical and physical changes to materials, coolants, and fuels in future nuclear energy systems.

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APPENDIX A: WORKSHOP PARTICIPANTS

Basic Research Needs for Future Nuclear Energy Workshop

Chair: Kelly Beierschmitt (Idaho National Laboratory)

Co-chairs: Michelle Buchanan (Oak Ridge National Laboratory)
Aurora Clark (Washington State University)
Ian Roberston (University of Wisconsin–Madison)

Basic Energy Sciences Team: Linda Horton, Materials Sciences and Engineering
Bruce Garrett, Chemical Sciences, Geosciences, and Biosciences
John Vetrano, Materials Sciences and Engineering
Philip Wilk, Chemical Sciences, Geosciences, and Biosciences
Katie Runkles, BES Administrative Lead

Plenary Speakers:

Kevan Weaver, TerraPower
John Herczeg, DOE –Office of Nuclear Energy
Sheng Dai, Oak Ridge National Laboratory
Laura Gagliardi, University of Minnesota
Robin Grimes, Imperial College

Panel A: Design and Discovery of Coolants and Liquid Fuels

Chairs: Phillip Britt, Oak Ridge National Laboratory; Alexandra Navrotsky, University of California–Davis

William (Bill) Casey, University of California–Davis
Sue Clark, Pacific Northwest National Laboratory[w]
Richard Crooks, University of Texas–Austin
Nicolas Dacheux, University of Montpellier
Dave Dixon, University of Alabama[w]
David Grills, Brookhaven National Laboratory
Ed Maginn, University of Notre Dame
Vic Maroni, Argonne National Laboratory (retired)[w]
Amy Marschilok, SUNY Stony Brook
Jenifer Shafer, Colorado School of Mines[w]
Kumar Sridharan, University of Wisconsin–Madison
Michael Toney, SLAC National Accelerator Laboratory[c]

Panel B: Physics and Chemistry of Interfaces

Chairs: Amit Misra, University of Michigan; James Wishart, Brookhaven National Laboratory

Niaz Abdolrahim, University of Rochester
Peter Anderson, Ohio State University
Ying Chen, Rensselaer Polytechnic Institute[c]
Samrat Choudhury, University of Idaho
Tanja Cuk, University of California–Berkeley/Lawrence Berkeley National Laboratory
Vinayak Dravid, Northwestern University[c]
Jian Gan, Idaho National Laboratory
Simerjeet Gill, Brookhaven National Laboratory
Khalid Hattar, Sandia National Laboratories[w]
Jessica Krogstad, University of Illinois, Urbana-Champaign
Jay LaVerne, University of Notre Dame
Emmanuelle Marquis, University of Michigan
Thom Orlando, Georgia Institute of Technology[w]

c indicates Crosscutting Themes; *w* indicates writer

Nikolai Petrik, Pacific Northwest National Laboratory
Simon Pimblott, University of Manchester
Guangwen Zhou, SUNY Binghamton

Panel C: Understanding Behavior at Coupled Extremes

Chairs: Bruce Mincher, Idaho National Laboratory; Izabela Szlufarska, University of Wisconsin

Jeremy Busby, Oak Ridge National Laboratory
Christopher Dares, Florida International University[w]
Andreas Geist, Karlsruhe Institute of Technology
Peter Hosemann, University of California–Berkeley[w]
Yutai Katoh, Oak Ridge National Laboratory
Maik Lang, University of Tennessee–Knoxville[c]
Laurence Marks, Northwestern University
Mathew Mathew, University of Illinois–Chicago
Steve Mezyk, California State University–Long Beach
Mikael Nilsson, University of California–Irvine
Subramanian Sankaranarayanan, Argonne National Laboratory
John Scully, University of Virginia
Gary Was, University of Michigan[c]
Clara Wren, Western University
Peng Xu, Westinghouse

Panel D: Design and Discovery of Structural Materials and Solid Fuels

Chairs: Peter Burns, Notre Dame University; Peter Tortorelli, Oak Ridge National Laboratory (retired)

Todd Allen, University of Wisconsin/Idaho National Laboratory[c]
Mark Asta, University of California–Berkeley/Lawrence Berkeley National Laboratory
Pascal Bellon, University of Illinois, Urbana-Champaign
Don Brown, Los Alamos National Laboratory[c]
T. S. Byun, Pacific Northwest National Laboratory
Laura Gagliardi, University of Minnesota
Michele Manuel, University of Florida
Mitchell Meyer, Idaho National Laboratory
Albert Migliori, Los Alamos National Laboratory
Tina Nenoff, Sandia National Laboratories[w]
Kurt Terrani, Oak Ridge National Laboratory[w]
Jason Trelewicz, SUNY Stony Brook[c]
James Warren, National Institute of Standards and Technology
Yanwen Zhang, Oak Ridge National Laboratory
Steve Zinkle, University of Tennessee–Knoxville

***c* indicates Crosscutting Themes; *w* indicates writer**

Panel E: Crosscutting Themes

Chairs: Paul Fenter, Argonne National Laboratory; Andy Gewirth, University of Illinois, Urbana-Champaign; Brian Wirth, University of Tennessee–Knoxville

Todd Allen, University of Wisconsin/Idaho National Laboratory[d]
Don Brown, Los Alamos National Laboratory[d]
Ying Chen, Rensselaer Polytechnic Institute[b]
Vinayak Dravid, Northwestern University[b]
Daniel Gianola, University of California–Santa Barbara
Maik Lang, University of Tennessee–Knoxville[c]
Michael Toney, SLAC National Accelerator Laboratory[a/w]
Jason Trelewicz, SUNY Stony Brook[d/w]
Gary Was, University of Michigan[c]

***a*, *b*, *c*, and *d* indicate the theme panel that the individual represents; *w* indicates writer**

Invited Participants

Niaz Abdolrahim, University of Rochester
Todd Allen, University of Wisconsin/Idaho National Laboratory
Peter Anderson, Ohio State University
Mark Asta, University of California–Berkeley/Lawrence Berkeley National Laboratory
Kelly Beierschmitt, Idaho National Laboratory
Pascal Bellon, University of Illinois, Urbana-Champaign
Phillip Britt, Oak Ridge National Laboratory
Don Brown, Los Alamos National Laboratory
Michelle Buchanan, Oak Ridge National Laboratory
Peter Burns, University of Notre Dame
Jeremy Busby, Oak Ridge National Laboratory
T. S. Byun, Pacific Northwest National Laboratory
William (Bill) Casey, University of California–Davis
Ying Chen, Rensselaer Polytechnic Institute
Samrat Choudhury, University of Idaho
Aurora Clark, Washington State University
Sue Clark, Pacific Northwest National Laboratory
Richard Crooks, University of Texas–Austin
Tanja Cuk, University of California–Berkeley/ Lawrence Berkeley National Laboratory
Nicolas Dacheux, University of Montpellier
Sheng Dai, Oak Ridge National Laboratory
Christopher Dares, Florida International University
Dave Dixon, University of Alabama
Vinayak Dravid, Northwestern University
Paul Fenter, Argonne National Laboratory
Laura Gagliardi, University of Minnesota
Jian Gan, Idaho National Laboratory
Andreas Geist, Karlsruhe Institute of Technology
Andy Gewirth, University of Illinois, Urbana-Champaign
Daniel Gianola, University of California–Santa Barbara
Simerjeet Gill, Brookhaven National Laboratory
David Grills, Brookhaven National Laboratory
Robin Grimes, Imperial College London
Khalid Hattar, Sandia National Laboratories
John Herczeg, DOE–Nuclear Energy
Peter Hosemann, University of California–Berkeley
Yutai Katoh, Oak Ridge National Laboratory
Jessica Krogstad, University of Illinois, Urbana-Champaign
Maik Lang, University of Tennessee–Knoxville
Jay LaVerne, University of Notre Dame
Ed Maginn, University of Notre Dame
Michele Manuel, University of Florida
Laurence Marks, Northwestern University
Vic Maroni, Argonne National Laboratory (retired)

Emmanuelle Marquis, University of Michigan
Amy Marschilok, SUNY Stony Brook
Mathew Mathew, University of Illinois–Chicago
Mitchell Meyer, Idaho National Laboratory
Steve Mezyk, California State University–Long Beach
Albert Migliori, Los Alamos National Laboratory
Bruce Mincher, Idaho National Laboratory
Amit Misra, University of Michigan
Alexandra Navrotsky, University of California–Davis
Tina Nenoff, Sandia National Laboratories
Mikael Nilsson, University of California–Irvine
Thom Orlando, Georgia Institute of Technology
Nikolai Petrik, Pacific Northwest National Laboratory
Simon Pimblott, University of Manchester
Ian Robertson, University of Wisconsin
Subramanian Sankaranarayanan, Argonne National Laboratory
John Scully, University of Virginia
Jenifer Shafer, Colorado School of Mines
Kumar Sridharan, University of Wisconsin
Izabela Szlufarska, University of Wisconsin
Kurt Terrani, Oak Ridge National Laboratory
Michael Toney, SLAC National Accelerator Laboratory
Peter Tortorelli, Oak Ridge National Laboratory (retired)
Jason Trelewicz, SUNY Stony Brook
James Warren, National Institute of Standards and Technology
Gary Was, University of Michigan
Kevan Weaver, TerraPower
Brian Wirth, University of Tennessee–Knoxville
James Wishart, Brookhaven National Laboratory
Clara Wren, Western University
Peng Xu, Westinghouse
Yanwen Zhang, Oak Ridge National Laboratory
Guangwen Zhou, SUNY Binghamton
Steve Zinkle, University of Tennessee–Knoxville

Invited Observers

Tom Arsenlis, Lawrence Livermore National Laboratory
Ilke Arslan, Pacific Northwest National Laboratory
Jeff Binder, Argonne National Laboratory
Daniel Clark, DOE–Fusion Energy Science
Peter Collins, Ames Laboratory
Doug Crawford, Idaho National Laboratory
Glen Crawford, DOE–High Energy Physics
Teresa Crockett, DOE–Basic Energy Sciences
Matthew Denman, Sandia National Laboratories

Remi Dingreville, Sandia National Laboratories
Janelle Eddins, DOE–Nuclear Energy
Phil Edmondson, Oak Ridge National Laboratory
Greg Fiechtner, DOE–Basic Energy Sciences
Peter Fischer, Lawrence Berkeley National Laboratory
Luke Fletcher, SLAC National Accelerator Laboratory
Brenda Garcia-Diaz, Savannah River National Laboratory
Marc Garland, DOE–Nuclear Physics
Bruce Garrett, DOE–Basic Energy Sciences
Mary Gillespie, DOE–Nuclear Energy
George Goff, Los Alamos National Laboratory
Matthias Graf, DOE–Basic Energy Sciences
Linda Horton, DOE–Basic Energy Sciences
Jim Horwitz, DOE–Basic Energy Sciences
David Hurley, Idaho National Laboratory
Erfan Ibrahim, National Renewable Energy Laboratory
Alan Icenhour, Oak Ridge National Laboratory
Tatiana Ivanova, Nuclear Science Committee, Organisation for Economic Co-operation and Development
Hesham Khalifa, General Atomics
Stephen Kung, DOE–Nuclear Energy
Harriet Kung, DOE–Basic Energy Sciences
Randall Laviolette, DOE–Advanced Scientific Computing Research
Susan Lesica, DOE–Nuclear Energy
Meimei Li, Argonne National Laboratory
Diana Li, DOE–Nuclear Energy
Apurva Mehta, SLAC National Accelerator Laboratory
Tom Miller, DOE–Nuclear Energy
Raul Miranda, DOE–Basic Energy Sciences
Jamie Morris, Oak Ridge National Laboratory
Gene Nardella, DOE–Fusion Energy Science
Philip Parilla, National Renewable Energy Laboratory
Chuck Peden, DOE–Basic Energy Sciences
Mark Pederson, DOE–Basic Energy Sciences
Mike Pellin, Argonne National Laboratory
James Rhyne, DOE–Basic Energy Sciences
Katie Runkles, DOE–Basic Energy Sciences
Tom Russell, DOE–Basic Energy Sciences
Jim Rustad, DOE–Basic Energy Sciences
Suibel Schuppner, DOE–Nuclear Energy
Andy Schwartz, DOE–Basic Energy Sciences
Viviane Schwartz, DOE–Basic Energy Sciences
Tom Settersen, DOE–Basic Energy Sciences
Nick Smith, Southern Company
Mark Spitler, DOE–Basic Energy Sciences
Dave Sprouster, Brookhaven National Laboratory
Chris Stanek, Los Alamos National Laboratory

Petr Sushko, Pacific Northwest National Laboratory
Thiyaga Thiyagarajan, DOE–Basic Energy Sciences
Patrice Turchi, Lawrence Livermore National Laboratory
John Vetrano, DOE–Basic Energy Sciences
Philip Wilk, DOE–Basic Energy Sciences
Kevin Wilson, Lawrence Berkeley National Laboratory
Jason Wilson, Savannah River National Laboratory
Brenda Wyatt, Oak Ridge National Laboratory
Zhong, Brookhaven National Laboratory
Jane Zhu, DOE–Basic Energy Sciences

APPENDIX B: WORKSHOP AGENDA

BASIC RESEARCH NEEDS FOR

Future Nuclear Energy Workshop

Hilton Washington DC/Rockville Hotel ● August 9–11, 2017

Wednesday, August 9, 2017	
7:00 – 8:00 a.m.	Registration and breakfast
Opening Plenary Session — Plaza Ballroom	
8:00 – 8:15 a.m.	**BES Welcome and Workshop Charge** Harriet Kung, Associate Director of Science for Basic Energy Sciences
8:15 – 8:30 a.m.	**Chair Welcome and Workshop Structure** Kelly Beierschmitt, Idaho National Laboratory (workshop chair)
8:30 – 8:45 a.m.	**Introduction to Plenaries** Aurora Clark, Washington State University (workshop co-chair)
8:45 – 9:15 a.m.	**The Role of American Innovation in a Global Marketplace** Kevan Weaver, TerraPower
9:15 – 9:45 a.m.	**Nuclear Energy Needs in Basic Science to Support the Next Generation of Advanced Reactors** John Herczeg, DOE–Office of Nuclear Energy
9:45 – 10:15 a.m.	**Chemistry for Molten Salt Reactors—History and Perspectives** Sheng Dai, Oak Ridge National Laboratory
10:15 – 10:45 a.m.	Break
10:45 – 11:15 a.m.	Session chair: Ian Robertson, University of Wisconsin–Madison (workshop co-chair) **Theoretical and Computational Challenges for the Future of Nuclear Energy** Laura Gagliardi, University of Minnesota
11:15 – 11:45 a.m.	**The Future for Fuels and Materials** Robin Grimes, Imperial College
11:45 – 12:00 p.m.	Panel introductions—Michelle Buchanan, Oak Ridge National Laboratory (workshop co-chair)
12:00 – 1:30 p.m.	Working lunch
1:30 – 5:30 p.m.	**Parallel Panel Sessions**
Panel A	**Design and Discovery of Coolants and Liquid Fuels** *Phil Britt, Oak Ridge National Laboratory, and Alexandra Navrotsky, University of California–Davis*
Panel B	**Physics and Chemistry of Interfaces** *Amit Misra, University of Michigan, and Jim Wishart, Brookhaven National Laboratory*
Panel C	**Understanding Behavior at Coupled Extremes** *Bruce Mincher, Idaho National Laboratory, and Izabela Szlufarska, University of Wisconsin–Madison*
Panel D	**Design and Discovery of Structural Materials and Solid Fuels** *Peter Burns, University of Notre Dame, and Pete Tortorelli, Oak Ridge National Laboratory (retired)*
Crosscutting Themes	*Paul Fenter, Argonne National Laboratory; Andy Gewirth, University of Illinois, Urbana-Champaign; and Brian Wirth, University of Tennessee–Knoxville*

5:30 – 7:00 p.m.	Break for dinner (on own)
7:00 – 10:00 p.m.	**Parallel Panel Discussions** (continued)
Thursday, August 10, 2017	
7:00 – 8:00 a.m.	Breakfast
8:00 – 10:30 a.m.	**Parallel Panel Sessions** for discussion/preparation of preliminary reports
10:30 – 10:45 a.m.	Break
Plenary Session — Plaza Ballroom	
10:45 – 11:00 a.m.	**Report from Panel A**: Design and Discovery of Coolants and Liquid Fuels
11:00 – 11:15 a.m.	**Report from Panel B**: Physics and Chemistry of Interfaces
11:15 – 11:30 a.m.	**Report from Panel C**: Understanding Behavior at Coupled Extremes
11:30 – 11:45 p.m.	**Report from Panel D**: Design and Discovery of Structural Materials and Solid Fuels
11:45 – 12:00 p.m.	**Report from Crosscutting Themes**
12:00 – 1:30 p.m.	Working lunch
Plenary Session — Plaza Ballroom	
1:30 – 2:00 p.m.	Discussion of refined PRDs
2:00 – 5:30 p.m.	Breakout to panel/PRD discussions (continued)
5:30 – 7:00 p.m.	Break for dinner (on own)
7:00 – 10:00 p.m.	Panel/PRD discussions (continued) and preparation for final panel reports
Friday, August 11, 2017	
Plenary Session — Plaza Ballroom	
7:00 – 8:00 a.m.	Breakfast
8:00 – 8:30 a.m.	**Report from PRD 1**
8:30 – 9:00 a.m.	**Report from PRD 2**
9:00 – 9:30 a.m.	**Report from PRD 3**
9:30 – 9:45 a.m.	Break
9:45 – 10:15 a.m.	**Report from PRD 4**
10:15 – 10:45 a.m.	**Report from PRD 5**
10:45 – 11:45 a.m.	Discussion
11:45 – 12:00 noon	**Closing Remarks** Kelly Beierschmitt, Idaho National Laboratory
12:00 noon	**Workshop Adjourned**
Noon – 5:00 p.m.	Working lunch/writing (chairs, panel leads and designated writers)

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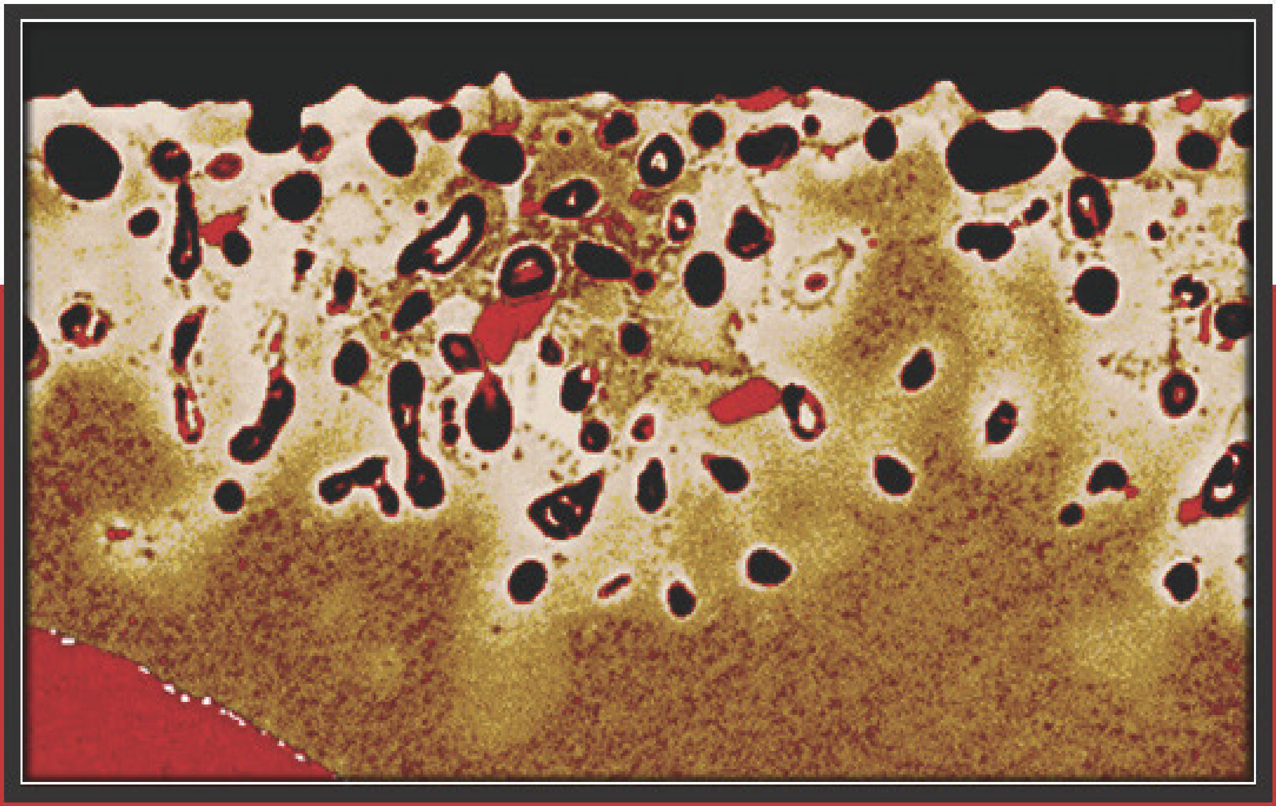

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