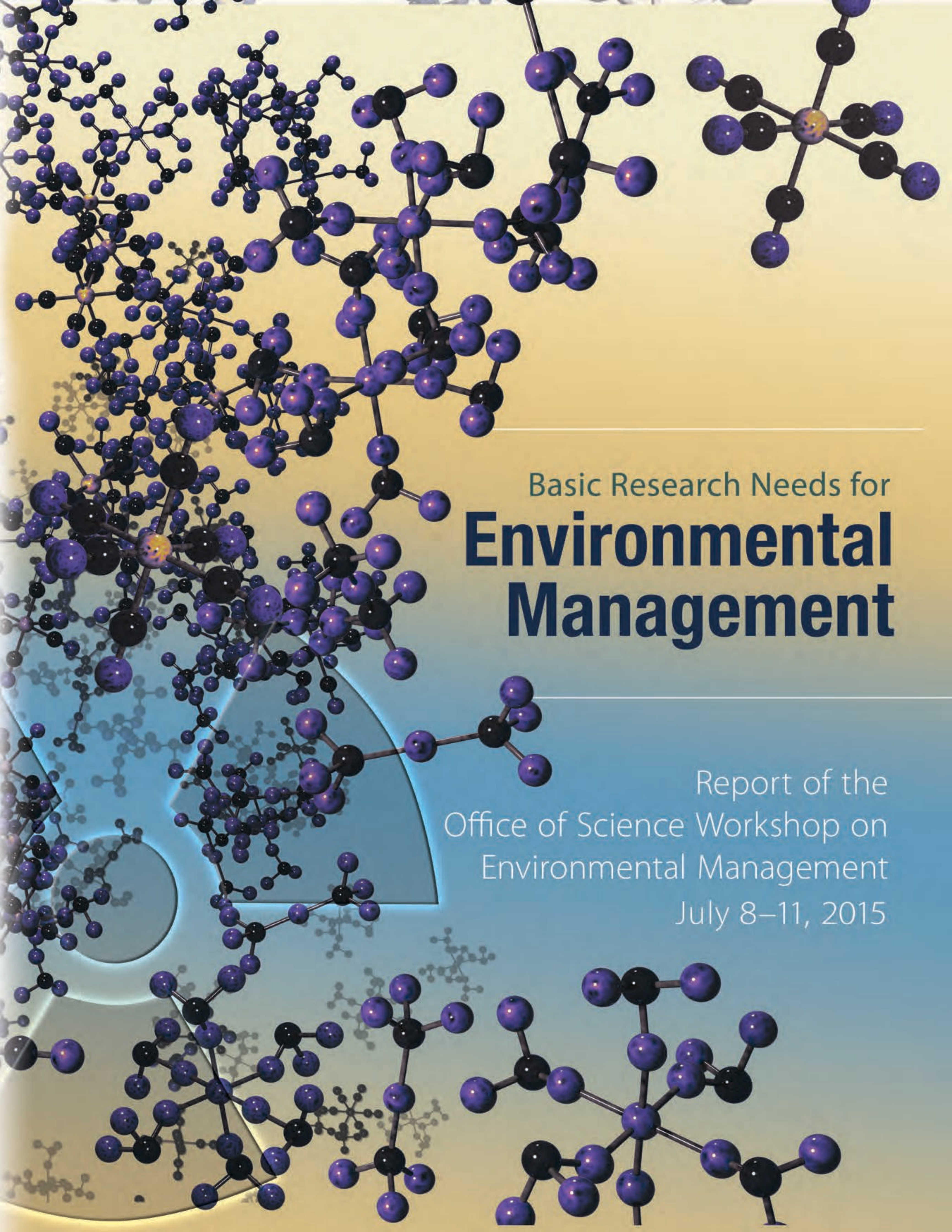


Basic Research Needs for

Environmental Management

Report of the
Office of Science Workshop on
Environmental Management
July 8–11, 2015

The cover depicts the chemical and physical complexity of the contents of hundreds of tanks, which collectively store hundreds of millions of liters of legacy wastes generated from weapons production and nuclear research at DOE sites. These wastes are highly heterogeneous and far from equilibrium due to high radioactivity, pH, and ionic strength. The myriad assemblages of soluble materials, suspended and precipitated solids, liquids, and gases are inhomogeneously distributed within the tanks and are poorly characterized, as signified by the undefined components of the depicted molecules. Characterizing these wastes is a critical first step in providing the scientific foundation required for developing revolutionary technologies for safe, efficient, and cost-effective remediation of the DOE sites.

Cover design by Andy Sproles, Oak Ridge National Laboratory

BASIC RESEARCH NEEDS FOR ENVIRONMENTAL MANAGEMENT

Report of the Office of Science Workshop on Environmental Management

Chair: Sue Clark, Pacific Northwest National Lab and Washington State University
Co-chairs: Michelle Buchanan, Oak Ridge National Lab
Bill Wilmarth, Savannah River National Lab

Panel Leads:

Waste Stream Characterization, Transformation and Separations
Jenifer Braley, Colorado School of Mines
Mark Antonio, Argonne National Lab

Waste Form
Gerald Frankel, Ohio State University
Jim Marra, Savannah River National Lab

Contaminant Fate and Transport in Geological Environments
David Cole, Ohio State University
Susan Hubbard, Lawrence Berkeley National Lab

Crosscutting Research
Todd Allen, Idaho National Lab
Aurora Clark, Washington State University

Office of Science Leads:

Andrew Schwartz, Basic Energy Sciences
David Lesmes, Biological and Environmental Research
Randall Laviolette, Advanced Scientific Computing Research

Special Assistance:

Technical: Kurt Gerdes, Environmental Management
John Miller, Basic Energy Sciences
Rod Rimando, Environmental Management
John Vetrano, Basic Energy Sciences

Administrative: Katie Runkles, Basic Energy Sciences
Alison Park, Pacific Northwest National Lab
Tammy Click, Oak Ridge Institute for Science and Education

Publication: Kristin Manke, Pacific Northwest National Lab
Jan Haigh, Pacific Northwest National Lab
Heather Culley, Pacific Northwest National Lab

This report is available on the web at
http://science.energy.gov/~/media/bes/pdf/reports/files/BRNEM_rpt.pdf

Office of Science
Department of Energy
February 2016

DISCLAIMER

CONTENTS

FIGURES

SIDEBARS

ACRONYMS AND ABBREVIATIONS

CSSX	caustic-side solvent extraction
DLVO	Deryaguin-Landau-Verwey-Overbeek
DOE	US Department of Energy
EM	Office of Environmental Management
PRD	Priority Research Direction
PUREX	plutonium-uranium extraction

EXECUTIVE SUMMARY

One of the US Department of Energy's (DOE) biggest challenges today is cleanup of the legacy resulting from more than half a century of nuclear weapons production. The research and manufacturing associated with the development of the nation's nuclear arsenal has left behind staggering quantities of highly complex, highly radioactive wastes and contaminated soils and groundwaters. Based on current knowledge of these legacy problems and currently available technologies, DOE projects that hundreds of billions of dollars and more than 50 years of effort will be required for remediation.

Over the past decade, DOE's progress towards cleanup has been stymied in part by a lack of investment in basic science that is foundational to innovation and new technology development. During this decade, amazing progress has been made in both experimental and computational tools that have been applied to many energy problems such as catalysis, bioenergy, solar energy, etc. Our abilities to observe, model, and exploit chemical phenomena at the atomic level along with our understanding of the translation of molecular phenomena to macroscopic behavior and properties have advanced tremendously; however, remediation of DOE's legacy waste problems has not yet benefited from these advances because of the lack investment in basic science for environmental cleanup.

Advances in science and technology can provide the foundation for completing the cleanup more swiftly, inexpensively, safely, and effectively. The lack of investment in research and technology development by DOE's Office of Environmental Management (EM) was noted in a report by a task force to the Secretary of Energy's Advisory Board (SEAB 2014). Among several recommendations, the report suggested a workshop be convened to develop a strategic plan for a "fundamental research program focused on developing new knowledge and capabilities that bear on the EM challenges." This report summarizes the research directions identified at a workshop on Basic Research Needs for Environmental Management. This workshop, held July 8-11, 2015, was sponsored by three Office of Science offices: Basic Energy Sciences, Biological and Environmental Research, and Advanced Scientific Computing Research. The workshop participants included 65 scientists and engineers from universities, industry, and national laboratories, along with observers from the DOE Offices of Science, EM, Nuclear Energy, and Legacy Management.

As a result of the discussions at the workshop, participants articulated two Grand Challenges for science associated with EM cleanup needs. They are as follows:

Interrogation of Inaccessible Environments over Extremes of Time and Space

Whether the contamination problem involves highly radioactive materials in underground waste tanks or large volumes of contaminated soils and groundwaters beneath the Earth's surface, characterizing the problem is often stymied by an inability to safely and cost effectively interrogate the system. Sensors and imaging capabilities that can operate in the extreme environments typical of EM's remaining cleanup challenges do not exist. Alternatively, large amounts of data can sometimes be obtained about a system, but appropriate data analytics tools are lacking to enable effective and efficient use of all the information for performance regression or prediction. Research into new approaches for remote and in situ sensing, and new algorithms for data analytics are critically needed. Depending on the cleanup problem, these new approaches must span temporal and spatial scales—from seconds to millennia, from atoms to kilometers.

Understanding and Exploiting Interfacial Phenomena in Extreme Environments

While many of EM's remaining cleanup problems involve unprecedented extremes in complexity, an additional layer is provided by the numerous contaminant forms and their partitioning across interfaces in these wastes, including liquid-liquid, liquid-solid, and others. For example, the wastes in the high-level radioactive waste tanks can have consistencies of paste, gels, or Newtonian slurries, where water behaves more like a solute than a solvent. Unexpected chemical forms of the contaminants and radionuclides partition to unusual solids, colloids, and other phases in the tank wastes, complicating their efficient separation. Mastery of the chemistry controlling contaminant speciation and its behavior at the solid-liquid and liquid-liquid interfaces in the presence of large quantities of ionizing radiation is needed to develop improved waste treatment approaches and enhance the operating efficiencies of treatment facilities. These same interfacial processes, if understood, can be exploited to develop entirely new approaches for effective separations technologies, both for tank waste processing and subsurface remediation.

Based on the findings of the technical panels, six Priority Research Directions (PRDs) were identified as the most urgent scientific areas that need to be addressed to enable EM to meet its mission goals. All of these PRDs are also embodied in the two Grand Challenges. Further, these six PRDs are relevant to all aspects of EM waste issues, including tank wastes, waste forms, and subsurface contamination. These PRDs include:

- Elucidating and exploiting complex speciation and reactivity far from equilibrium
- Understanding and controlling chemical and physical processes at interfaces
- Harnessing physical and chemical processes to revolutionize separations
- Mechanisms of materials degradation in harsh environments
- Mastering hierarchical structures to tailor waste forms
- Predictive understanding of subsurface system behavior and response to perturbations.

Two recurring themes emerged during the course of the workshop that cut across all of the PRDs. These crosscutting topics give rise to Transformative Research Capabilities. The first such capability, *Multidimensional characterization of extreme, dynamic, and inaccessible environments*, centers on the need for obtaining detailed chemical and physical information on EM wastes in waste tanks and during waste processing, in wastes forms, and in the environment. New approaches are needed to characterize and monitor these highly hazardous and/or inaccessible materials in their natural environment, either using in situ techniques or remote monitoring. These approaches are particularly suited for studying changes in the wastes over time and distances, for example. Such in situ and remote techniques are also critical for monitoring the effectiveness of waste processes, subsurface transport, and long-term waste form stability. However, far more detailed information will be needed to obtain fundamental insight into materials structure and molecular-level chemical and physical processes required for many of the PRDs. For these studies, samples must be retrieved and studied ex situ, but the hazardous nature of these samples requires special handling. Recent advances in nanoscience have catalyzed the development of high-sensitivity characterization tools—many of which are available at DOE user facilities, including radiological user facilities—and the means of handling ultrasmall samples, including micro- and nanofluidics and nanofabrication tools. These advances open the door to obtaining unprecedented information that is crucial to formulating concepts for new technologies to complete EM's mission.

The sheer magnitude of the data needed to fully understand the complexity of EM wastes is daunting, but it is just the beginning. Additional data will need to be gathered to both monitor and predict changes—in tank wastes, during processing, in waste forms and in the subsurface over broad time and spatial scales. Therefore, the second Transformative Research Capability, *Integrated simulation and data-enabled discovery*, identified the need to develop curated databases and link experiments and theory through big-deep data methodologies. These state-of-the-art capabilities will be enabled by high-performance computing resources available at DOE user facilities.

The foundational knowledge to support innovation for EM cannot wait as the tank wastes continue to deteriorate and result in environmental, health, and safety issues. As clearly stated in the 2014 Secretary of Energy Advisory Board report, completion of EM's remaining responsibilities will simply not be possible without significant innovation and that innovation can be derived from use-inspired fundamental research as described in this report. The breakthroughs that will evolve from this investment in basic science will reduce the overall risk and financial burden of cleanup while also increasing the probability of success. The time is now ripe to proceed with the basic science in support of more effective solutions for environmental management. The knowledge gleaned from this basic research will also have broad applicability to many other areas central to DOE's mission, including separations methods for critical materials recovery and isotope production, robust materials for advanced reactor and steam turbine designs, and new capabilities for examining subsurface transport relevant to the water/energy nexus.

INTRODUCTION

During World War II and the Cold War, the US Department of Energy (DOE) and its predecessor agencies produced significant quantities of materials for the nation's arsenal of nuclear weapons. This large-scale production involved processes that were conducted in multiple government-owned facilities distributed across the United States. Processes included uranium mining and milling; uranium enrichment; fuel and target fabrication; irradiation in nuclear reactors; chemical separations; production of uranium and plutonium oxide, alloys, and other metallic products; and management of the wastes associated with these processes. These large-scale industrial activities produced a tremendous quantity of wastes in many forms. In addition, there were intentional and accidental releases of radioactivity and hazardous materials to the environment.

Nuclear weapons production in the United States ceased in the late 1980s and early 1990s, and the facilities were placed in varying degrees of disposition as the Cold War came to an end. At this time, DOE's focus turned towards remediation of the weapons legacy that resulted from the production and research operations. DOE's Office of Environmental Management (EM) was charged with the legacy cleanup. As EM began its efforts, at least 29 states were home to one or more of the original 107 legacy sites that made up the nationwide nuclear weapons complex (DOE 1997). Since EM began its efforts in 1989, 91 of these original sites have been remediated, costing over $150 billion. However, these sites were relatively small and not extensively contaminated. In contrast, the remaining 16 sites present exceedingly greater technological challenges, with highly contaminated materials and wastes as well as extensive environmental contamination. The states left with the largest quantities of legacy materials and facilities are South Carolina (Savannah River Site), Tennessee (Oak Ridge Reservation), and Washington (Hanford Site).

EM's remaining cleanup challenges are simply staggering in their technical complexity and will take decades to resolve. As EM plans for these remaining challenges, it projects that completion of its mission will require at least another 50 years and at least $235 billion. Nearly half of the estimated funding is required for processing millions of liters of highly radioactive liquid wastes that are currently stored in over 200 underground tanks. Based on historical funding levels of $6 billion per year, EM currently estimates a budget shortfall of at least $28 billion. A recent report by the Secretary of Energy Advisory Board stated, "Finding ways to reduce the aggregate cost, to do the job more effectively and safely, and to speed up the work will clearly serve the American public. Technology offers that opportunity. Moreover, new technology is necessary because there are significant challenges associated with the cleanup work ahead. In fact, without the development of new technology, it is not clear that the cleanup can be completed satisfactorily or at any reasonable cost" (SEAB 2014).

In the early years (before 2000), about 4 percent of EM's budget was invested in research and development. For various reasons since that time, EM's investment in research and development has plummeted such that in 2014, the budget for technology development was only 0.2 percent of EM's budget. Over the past decade, significant advances have been made in experimental and computational tools to enable the development of foundational knowledge of molecular phenomena. In other aspects of DOE's technology programs, amazing progress has occurred in the ability to link molecular phenomena to macroscopic observables over time and space. However, due to the lack of investment in basic research for technology development by EM, waste cleanup efforts have not benefited from these advances; this lack of investment has limited innovation and new technology development for cleanup. This presents the opportunity to invest in basic science to provide a foundation for new cleanup approaches. Although there is urgency in moving forward on DOE cleanup, the timeframe for completion allows for investment in use-inspired basic science associated with bottlenecks in the cleanup processes. Such investment will serve the American public by reducing aggregate costs via increased efficiencies and efficacies of remediation. Broader impacts of the research needs described in this report include other areas central to DOE's mission. From these efforts, new separations methods may be realized for critical materials recovery and isotope production. In addition, this work may lead to more robust materials for advanced reactor and steam turbine designs, and new capabilities for examining subsurface transport relevant to the water/energy nexus.

Transformative Opportunities to Innovate Revolutionary New Cleanup Approaches

The pursuit of fundamental research that bears on EM challenges could advance understanding in important areas and pave the way for both incremental improvements and high-impact technology that would significantly reduce the magnitude of the cleanup cost and schedule. As noted by a Secretary of Energy Advisory Board task force, EM has lacked a vigorous effort to pursue use-inspired fundamental research and develop technologies that are outside of their day-to-day program over the last decade (SEAB 2014). Such a vigorous research effort must target big challenges that hold the promise of breakthrough performance. This situation has hampered opportunities to develop game-changing technologies that could significantly speed cleanup, reduce cost, and/or improve effectiveness. Given the expected duration of the work, there is ample time to develop and deploy such technologies or to adapt and improve technologies from other industries or applications.

One example of a missed opportunity relates to the high-level radioactive wastes currently stored in tanks at the Hanford Site in Washington State, the Savannah River Site in South Carolina, and the West Valley Nuclear Site in New York. Nearly half of EM's cleanup funding is currently being spent to address the required processing of about 300 million liters of highly radioactive wastes that are distributed between these sites. Large quantities of highly radioactive materials must be processed and effectively immobilized in waste forms that will endure storage for many hundreds of years. However, the contents of these tanks represent some of the most complex and hazardous mixtures known on Earth, containing hundreds of curies of radioactivity and a multitude of chemical components, including soluble materials, suspended solids, precipitates (sludge), and gases. The contents of these tanks are highly alkaline, contain concentrated electrolytes, and are highly radioactive. Further, the wastes within a given tank are stratified and very heterogeneous; they vary tremendously between tanks; and are changing with time due to radiation effects and chemical reactivity. Even understanding the most basic information, such as the full range of species present in the tanks, is a significant challenge. The stability of the tanks themselves is a great concern because the extreme conditions inside the tanks has promoted corrosion and failure of tank materials. Some of the tanks have leaked over the decades and contributed to contamination of tens of square miles of groundwater and soils with radioactive and other hazardous wastes that require monitoring and/or remediation with additional associated costs.

While the challenges associated with high-level radioactive wastes and other EM cleanup problems may at first seem insurmountable, major technology breakthroughs are possible if they are based on a fundamental understanding of the effects of extreme environments on the chemistry of the system and the materials within the system. By understanding the demands placed on the contaminant species and associated materials by extreme environments, particularly at the atomic and molecular levels, scientists and engineers can begin to exploit previously unknown and unrealized chemistries, which can lead to the development of next-generation, disruptive technologies. Over the last decade, incredible advances in computational ability, understanding of nanoscience, and amazing increases in resolution for dynamic imaging and other spectroscopies have occurred. Unfortunately, the EM cleanup mission has not yet benefited from these advances. Applying these revolutionary new tools to EM's problems can create an entirely new paradigm for legacy waste cleanup.

Defining Basic Research Needs for Environmental Management

One of the recommendations of the Secretary of Energy Advisory Board task force was for DOE's Office of Science to conduct a workshop to develop a strategic research plan to inform a plan for a "fundamental research program focused on developing new knowledge and capabilities that bear on the EM challenges" (SEAB 2014). This report summarizes the research directions identified at a workshop titled Basic Research Needs for Environmental Management. This workshop, held July 8-11, 2015, was sponsored by three Office of Science offices: Basic Energy Sciences, Biological and Environmental Research, and Advanced Scientific Computing Research, and was supported by EM. Prior to the workshop, experts who have extensive knowledge of EM sites, especially Savannah River and Hanford Sites, prepared a technology resource document, *Technology and Applied R&D Needs for Environmental Management* (Appendix A), which provided the foundation on which the discussions of the workshop were initiated (Appendix B). The workshop participants included 65 scientists and engineers from universities, industry, and national laboratories, along with observers from the DOE Office of Science, EM, and the Offices of Nuclear Energy and Legacy Management.

The workshop began with a plenary session that outlined the current state of the art and technology gaps that impact EM's mission. The participants divided into panels to assess promising basic research opportunities that form the basis of this report. Panel 1, *Waste Stream Characterization, Transformation, and Separations*, examined research needs in measurement and characterization of waste streams, actinide and fission product chemistry in synthetic and natural environments, and separation approaches. Panel 2, *Waste Forms*, examined issues related to the stability of vitrified wastes, ceramics, other waste forms, and to metal waste containers (including the tanks) resulting from stresses induced by radiation, temperature, corrosion, and other chemical reactions. Panel 3, *Contaminant Fate and Transport in Geological Environments*, examined issues related to understanding the relevant subsurface environment; multiphase flow and transport; and measurement, modeling and verification, and systems approaches. A fourth panel was formed to assess common basic research needs that cut across the three technology panels. The goal of these panels was to identify specific Priority Research Directions (PRDs) that would lead to the development of revolutionary new technologies to advance EM's mission with respect to effectiveness, cost, and safety.

The sheer complexity of stored tank wastes presents a huge technology challenge for EM. The many hundreds of chemicals in the tanks exist as solids, liquids, and gases in an environment that is far from equilibrium. The resulting mixtures are dynamic in composition, driven by localized inhomogeneities and the presence of highly ionizing radiation and electrons and radicals that exist due to extremes in alkalinity and ionic strength. Thus, the specific forms of many radionuclides in these tanks are poorly understood and it is essential to understand the chemistries of these species before efficient approaches for separating these highly radiative species can be devised. Further, the dynamic environments of these tank wastes require understanding the interactions of species across broad length and time scales, from atomic to meter scales and from fractions of a second to years. Understanding the chemical interactions occurring in the tanks will also provide insight into macroscale phenomena, such as waste stream rheology, slurry agglomeration, and precipitation, which will help prevent pipe clogging, precipitation, and filter fouling and thus improve solution handling as these materials are being processed.

Without a doubt, the biggest technical bottleneck that must be addressed is the separations of the most highly hazardous radioactive materials from the tank solutions. To complete EM's mission in an efficient and cost-effective manner, a new generation of separation materials is critically needed. These materials must be extremely robust—with high performance lifetimes and recyclability—and capable of withstanding high levels of ionization radiation and alkalinity. Recent advances in nanoscience may lead to the design of new materials with specific architectures to yield materials with tailored pores or supramolecular structures that are highly selective for the targeted chemical species. One could even imagine materials designed to remove multiple species in a single step, rather than needing to have costly, sequential processes. To realize this potential, however, fundamental understanding of the chemical interactions of the targeted species with the separations materials is mandatory.

Processing the tank wastes will also require vessels, piping, and other materials designed to operate reliably in the extreme conditions that exist in the waste tank solutions. Failures of these materials can result in costly unexpected interruptions in processing and unintended release of these materials into the environment. Understanding the interactions of the tank waste solutions with exposed materials at the atomic scale is critical in elucidating the failure of these materials. This knowledge will, in turn, serve as the basis for development of new materials that will meet the full range of requirements needed for waste handling, processing, and long-term storage.

Once the highly hazardous materials are isolated, they must be prepared for disposal to ensure long-term safety of human health and the environment. Unfortunately, the extreme complexity of the tank wastes, and the variability from one tank to another, precludes a single approach for waste stabilization. Thus, new materials are needed to provide immobilization that is predictable over hundreds and thousands of years. This will require a fundamental understanding of the myriad processes that can cause deterioration and eventual failure of storage materials. In addition, the processes developed to isolate the highly hazardous materials must be closely coupled with the design of materials for long-term storage. Designing these processes and materials as a system will have an enormous impact on the development of efficient, predictable, and cost-effective protocols required to meet EM’s mission.

As processes are being developed for treating and long-term storage of tank wastes, leakage from these tanks continues to contaminate the environment on and surrounding DOE sites. Remediation of sites, estimated to include millions of liters of water and tens of million cubic meters of soil, requires understanding of subsurface processes and properties that influence the fate and transport of the contaminates. In addition, this knowledge will provide the scientific basis for developing next-generation remediation technologies for EM. A significant challenge is identifying the chemical form of radioactive contaminants in the subsurface environment, including the transformation of these materials by biogeochemical processes. This environment is immensely complex, with inorganic and organic species co-mingled with microbes and reactive solutes that can both control transport in the subsurface and modify the chemical state of the contaminant. Unfortunately, the complex processes that occur in the subsurface are poorly understood. This information is vitally important for comprehending and predicting the chemical, physical, and biological processes that control transport of contaminants in the environment and for developing effective methods for remediating soils and waters. For example, little is understood about the interfacial processes that control transport of materials through pores, especially low-permeability domains, in the subsurface. Further complicating these environments are transient perturbations such as extreme natural and human-made events. These events include floods, fires, and contaminant releases, among others. Understanding the fundamental transport of materials in the subsurface and the impact of transient effects is critically needed to obtain predictive models of how such events will affect management and remediation of contaminated soils and water.

The participants in the workshop panels noted that for the first time in history a combination of experimental and computational tools is available that has remarkable power and uniqueness suitable for exploring the characteristics of materials at length and time scales necessary to understand performance in extremes. Among them are high-intensity X-ray light sources, high-flux neutron sources, high-intensity, advanced microscopies (including optical, electron, and scanning probes), radiological facilities, and ultrascale computers, combined with modeling, simulation, and data visualization tools needed to take advantage of their power.

Summary of the Outcomes of the Workshop

As a result of the discussions at the workshop, two overarching Grand Challenges emerged, as outlined below.

Interrogation of inaccessible environments over extremes of time and space. Whether the contamination problem involves highly radioactive materials in underground waste tanks or large volumes of contaminated soils and groundwaters beneath the Earth's surface, characterizing the problem is often stymied by an inability to safely and cost effectively access the system. Sensors and imaging capabilities that can operate in the extreme environments typical of EM's remaining cleanup challenges do not exist. Alternatively, large amounts of data can sometime be obtained about a system, but appropriate data analytics tools are lacking to enable effective and efficient use of all of the information. Research into new approaches for remote and in situ sensing and new algorithms for data analytics are critically needed. Depending on the cleanup problem, these new approaches must span temporal problems from seconds to millennia and spatial scales from atoms to kilometers.

Understanding and exploiting interfacial phenomena in extreme environments. While many of EM's remaining cleanup problems involve unprecedented extremes in complexity, an additional layer is provided by the multitude of interfaces in these wastes including liquid-liquid, liquid-solid, and others. For example, tank wastes can have the consistency of peanut butter, where water behaves more like a solute than a solvent, and radionuclides can partition to solids, colloids, and other phases, complicating their efficient separation. A better understanding of contaminant behavior at the solid-liquid and liquid-liquid interfaces in the presence of large quantities of ionizing radiation is needed to develop improved waste treatment approaches and enhance the operating efficiencies of waste treatment facilities. However, these same interfacial processes, if understood, could form the basis of entirely new approaches for effective separations technologies, both for tank waste processing and subsurface remediation.

These Grand Challenges encompass six PRDs that were identified as the most urgent scientific areas that need to be addressed to enable EM to meet its mission goals. Further, these six PRDs are relevant to tank wastes, waste forms, and subsurface contamination. These PRDs are as follows:

- Elucidating and exploiting complex speciation and reactivity far from equilibrium
- Understanding and controlling chemical and physical processes at interfaces
- Harnessing physical and chemical processes to revolutionize separations
- Mechanisms of materials degradation in harsh environments
- Mastering hierarchical structures to tailor waste forms
- Predictive understanding of subsurface system behavior and response to perturbations.

Two recurring themes emerged during the course of the workshop, giving rise to Transformative Research Capabilities. The first opportunity, *Multidimensional characterization of extreme, dynamic, and inaccessible environments*, centers on the need for obtaining detailed chemical and physical information on EM wastes in waste tanks and during waste processing, in wastes forms, and in the environment. New approaches are needed to characterize and monitor these highly hazardous materials which are often inaccessible in their natural environment, either using in situ techniques or remote monitoring. These approaches are particularly suited for studying changes in the wastes over time and distances, for example. Such in situ and remote techniques are also critical for monitoring the effectiveness of waste processes, subsurface transport, and long-term waste stability. However, far more detailed information will be needed to obtain fundamental insight into materials structure and molecular-level chemical and physical processes required for many of the PRDs. For these studies, samples must be retrieved and studied ex situ, but the hazardous nature of these samples requires special handling. Recent advances in nanoscience have catalyzed the development of high-sensitivity characterization tools, many of which are available at DOE user facilities, as well as the means of handling ultrasmall samples including micro and nanofluidics and nanofabrication tools. These advances open the door to obtaining unprecedented information on EM wastes that are critically needed to formulate concepts for new technologies required for completing EM's mission.

The sheer magnitude of the data needed to fully understand the complexity of EM wastes is daunting, but it is just the beginning. Additional data will need to be gathered to both monitor and predict changes—in tank wastes, during processing, in waste forms, and in the subsurface over broad time and spatial scales. Therefore, the Transformative Research Capability, *Integrated simulation and data-enabled discovery*, identified the need to develop curated databases and link experiments and theory through big-deep data methodologies, where precisely targeted queries are made on large (petabytes and exabytes) data sets to provide real-time or near-real-time responses. These state-of-the-art capabilities will be enabled by high-performance computing resources available at DOE user facilities.

The foundational knowledge to support innovation for EM cannot wait as the tank wastes continue to deteriorate and result in environmental, health, and safety issues. As clearly stated in the 2014 Secretary of Energy Advisory Board report, completion of EM's remaining responsibilities will simply not be possible without significant innovation and that innovation can be derived from use-inspired fundamental research as described in this report. The breakthroughs that will evolve from this investment in basic science will reduce the overall risk and financial burden of cleanup while also increasing the probability of success. The time is now ripe to proceed with the basic science in support of more effective solutions for environmental management.

References

DOE – US Department of Energy. 1997. *Linking Legacies: Connecting the Cold War Nuclear Weapons Production Processes to their Environmental Consequences*. US Department of Energy, Washington, DC.

SEAB – Secretary of Energy Advisory Board. 2014. *Report of the Task Force on Technology Development for Environmental Management*. US Department of Energy, Washington, DC.

PANEL 1: WASTE STREAM CHARACTERIZATION, TRANSFORMATION, AND SEPARATIONS

Abstract

DOE EM is faced with the staggering responsibility of processing millions of liters of highly radioactive wastes to prepare them for geologic disposal. The chemistry of these wastes is highly heterogeneous and far from equilibrium due to high radioactivity, pH, and ionic strength. Current technologies fall far short of achieving this mission, and new approaches are critically needed to process these wastes efficiently and effectively. An essential first step is gaining a fundamental understanding of the multitude of chemical and physical processes that occur in these extreme environments, taking advantage of recent advances in nanoscience and new capabilities at DOE user facilities. Armed with this information, basic research can catalyze the development of wholly new processing technologies that can efficiently isolate hazardous materials from these wastes and safely meet EM's goals in a timely and cost-effective manner.

Introduction

EM has made substantial progress towards remediating many of its nuclear weapons and nuclear research sites; however, the remaining sites are vastly more complex and present significantly greater technical challenges and safety risks (Rimando, Jr. 2015). To safely complete the remaining cleanup, new approaches and technologies are needed to characterize, separate, and stabilize the wastes in forms that are acceptable for disposal. Conventional waste processing is expected to continue for at least several decades, which provides time for use-inspired research to support new approaches and technology development.

At the Hanford and Savannah River Sites, millions of liters of highly radioactive wastes are stored in aging waste tanks. At the Hanford Site, the compositions of the wastes vary from tank to tank because of upstream processes employed over the years. Further, the contents of various tanks were sometimes combined with other tanks. The wastes contain combinations of hundreds of chemical constituents in different forms. The chemical conditions of every tank are considered extreme due to high alkalinity, concentrated electrolytes, and large amounts of ionizing radiation. More details on the waste stream quantities and characteristics can be found in Appendix A.

In many cases, the processing of tank wastes is stymied because of the coupled complexity of the waste chemistry and associated safety risks. At the same time, the storage tanks are beyond their design life and, because some are now leaking, there is an urgent need for moving forward. Efficiencies are not optimized where wastes are being processed, which increases costs.

Waste characterization before processing is extremely expensive, primarily because the waste materials are highly radioactive (SRNL 2015). The radiation environment also causes surprises with respect to the behavior of the waste streams during processing. For example, solids in the actual waste streams are often more refractory than simulants that have not been exposed to the extreme conditions of the waste tanks (Russel et al. 2009). The costs associated with production of the waste forms and their ultimate disposal are extremely high, thus new methods are needed to increase separations efficiencies and optimize waste processing.

Over the past decades, DOE has developed some highly successful separations processes for these kinds of complex matrices, such as plutonium-uranium extraction (PUREX) to isolate plutonium and caustic-side solvent extraction (CSSX) to recover cesium (see Appendix A). Both of these processes are examples of the efficiencies and specificities that are possible, and both evolved from long-term investments in fundamental and use-inspired research programs. Additional, similar separations targeted at other key radionuclides are needed; for example, new extractive reagents for processes that combine high selectivities with favorable phase properties and resistance to or specific exploitation of radiolytic degradation. Some progress has been made in new approaches, such as oxidative caustic dissolution for the Hanford Site wastes, but lingering technical issues must be addressed before implementation. For this specific example, a more rigorous understanding of plutonium redox chemistry, speciation, coordination, and kinetics under highly caustic and radiolytic environments is needed. More generally, fundamental knowledge on the dynamics of interfacial chemistry of the waste solids and the associated fission products and other contaminants in radiation environments is essential to support safe and improved characterization and processing.

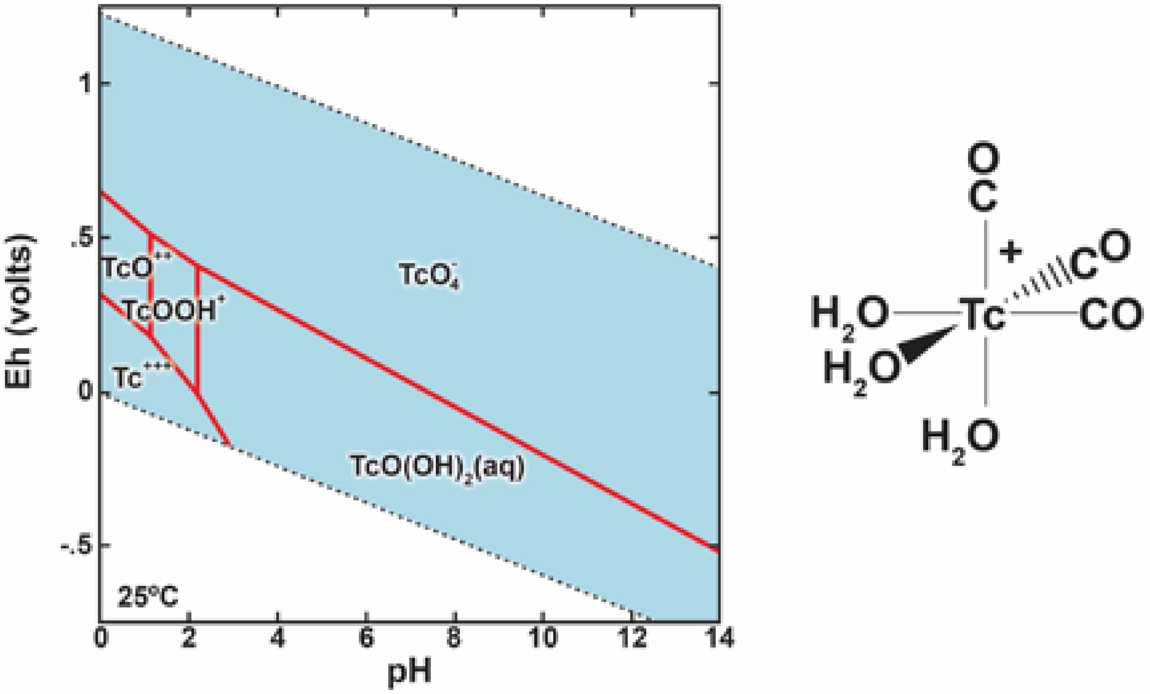
Fundamental Challenges and Research Opportunities

Any approach for processing stored tank wastes must deal with the extreme complexity of the wastes, which include numerous complicated assemblages of soluble materials, suspended and precipitated solids, liquids, and gases that are inhomogeneously distributed within the tanks. In most cases, water is limited in the wastes and acts as a solute rather than a solvent. A further complication is that these mixtures are dynamic—these assemblages have been aging in highly alkaline concentrated electrolytes and subjected to large quantities of ionizing radiation over many decades. These conditions have caused changes over time, including formation of unexpected electronic oxidation states in unusual chemical forms.

Under these conditions, risk-driving radionuclides (for example, plutonium, americium, curium, technetium, cesium, strontium, and iodine) have poorly understood chemistries that limit predictability of their behavior in process streams. Although recent studies on hydrated actinide cations such as $Th(H_2O)_{10}^{4+}$, $Pu(H_2O)_9^{3+}$, and $Cm(H_2O)_9^{3+}$ have significantly advanced the fundamental understanding of actinides in solution (Knope and Soderholm 2013), this behavior does not translate to the waste tank environment. Approaches developed for effective characterization and separations of tank wastes must address chemistries never before considered. Extending scientific knowledge of redox speciation in a radiation environment is essential. To gain more predictive capability, it is critical to determine valence, bonding, structure, and the phase of waste components in complex environments in the form of aqueous solutes, clusters, nanoparticles, sorbates, and incorporated ions in inorganic and organic materials. In addition to actinides and fission products, significant volumes of aluminum, chromium, phosphate, bismuth, and iron were commonly introduced into the solutions to improve initial separations processes. The presence of these additional materials complicates downstream processing and waste immobilization; thus, approaches for the efficient removal of these nonradioactive species are also needed. An example for species of technetium is provided in the sidebar. In this case, available thermodynamic data suggest that the species in the soluble fraction of the waste stream should be the pertechnetate anion (for example, TcO_4^-); the chemical form that is observed is a transient monovalent technetium cation in the form of either $Tc(CO)_3^+$ or $Tc(CO)_2NO^{2+}$ (Lukens et al. 2004).

Current understanding falls far short of providing the necessary foundation to develop reliable technologies for these extreme chemistries. Advances in fundamental science describing the speciation and chemical behavior of the actinides and fission products are essential to support waste characterization and separations technologies for the treatment of high-level radioactive wastes.

TECHNETIUM CARBONYL SPECIATION IN WASTE TANKS



Pourbaix diagram of technetium (left) and structure of a transient species suspected to be in the supernatant fraction of the Hanford Site tank wastes (Lukens et al. 2004; Pourbaix 1966; Serne and Rapko 2014). Images courtesy of Pacific Northwest National Laboratory.

The highly radioactive wastes in the tanks at the Hanford Site represent chemical systems that are far from equilibrium. Consequently, when the wastes are characterized before processing, unexpected species are found. For example, based on equilibrium thermodynamic calculations, the technetium (Tc) ion is expected to exist in the tank waste system as the pertechnetate species, TcO_4^-. Instead, a range of chemical forms is observed, with many of them being complete surprises. These surprises include monovalent technetium carbonyl species such as $Tc(CO)_3^+$ and $Tc(CO)_2NO^{2+}$ (see figure). Clearly, the conditions of the radioactive waste tanks are driving the formation and persistence of species that under equilibrium conditions are considered to be transient and unimportant. Designing processing schemes and separations for the highly radioactive waste streams must consider these species, yet the scientific basis for predicting them is currently lacking.

Understand Interactions across Multiple Scales

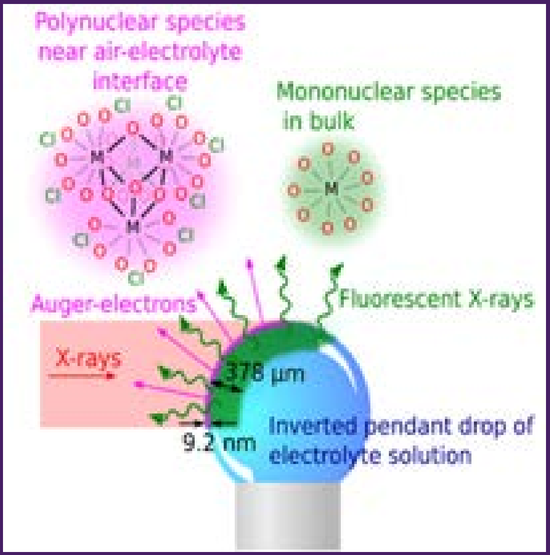
Predicting the behavior of high-level radioactive wastes and developing methods for their characterization and treatment requires an understanding of multiscale complexity and heterogeneity. This is where molecular, ionic, and electronic processes at interfaces (for example, solid-solid, liquid-solid, solid-gas, and liquid-liquid) in radiation environments often control interactions at the mesoscale. In turn, these interactions control a range of properties across various scales including colloid formation, particle transport, and flocculation or precipitation. The broad timescales of these dynamics are also equally important. Building a predictive capability for these interactions is a grand scientific challenge requiring development and application of new analytical and computational techniques. These methods could provide critical insights needed to understand and control the multitude of interactions in heterogeneous media across large variations and the three spatial dimensions and time. Advances in techniques for tank waste processing will also likely be useful for other EM mission applications, such as subsurface interfacial chemistry and contaminant transport.

Although knowledge of the collective phenomena is necessary for understanding interactions across scales, a first step involving individual system components is often necessary. This may mean isolating specific components for study that can lead to unintentional alteration of the system, including masking collective phenomena. For example, both amorphous and crystalline solids may play important roles in the behavior of certain wastes. These mixtures of solids require multimodal characterization such as X-ray scattering and diffraction as well as electron microscopy and optical spectroscopy. Advances in multimodal approaches that combine spectroscopic methods into a single measurement tool, as shown in the following sidebar, will likely prove very useful for capturing the collective behavior while also characterizing individual components. New analytical methods that can simultaneously take advantage of the individual chemical and physical properties of the heterogeneous mixtures (for example, differences in chemical state, density, and magnetic susceptibility) can also help minimize secondary waste volumes resulting from analysis. Also, analytical separations based on micro- and nano-fluidic approaches can lead to significant analytical cost savings due to waste minimization.

DOE scientific user facilities provide an exciting opportunity to probe structure and interactions at multiple length and timescales, in sometimes challenging operational situations such as those involving radioactivity. Neutron sources, X-ray light sources, electron microscopy centers, radiological user facilities, high-performance computing, and nanoscience facilities allow coupling theory with experiments done on multiple length scales. In particular, a number of remarkable developments have enabled X-ray and neutron scattering/reflectivity to probe structures at interfaces directly (Bera et al. 2015; Bu et al. 2014; Scoppola et al. 2015). Accomplishing this goal also requires developing new theory and algorithms implemented on exascale computer architectures to treat interactions in complex media across temporal and spatial scales. New computational approaches are also needed for searching, manipulating, and exploiting both existing and future data sets. Additionally, advances in uncertainty quantification could provide significant benefit to understanding the properties of waste streams and subsequent processing, including tank closure, filling, and monitoring.

Finally, understanding chemical interactions across scales of time and space will provide a molecular-scale explanation of poorly understood macroscale phenomena, such as waste stream rheology, slurry agglomeration, and control of precipitation. In turn, this understanding will provide the foundation for improving mixing systems, preventing pipe clogging and membrane fouling, and designing new, robust separations systems. This knowledge will reach far beyond high-level radioactive wastes and can be used to address many other complex heterogeneous processing problems, such as predicting subsurface colloid transport, designing coal slurry processing, and developing suspension-based biomass processing.

MULTIMODAL CHARACTERIZATION



Multimodal approach offers insights on metal cation speciation in and on liquid drops. Image reprinted (adapted) with permission from Polynuclear Speciation of Trivalent Cations near the Surface of an Electrolyte Solution, Mrinal K. Bera and Mark R. Antonio, *Langmuir*, 31 (19), 5432-5439 DOI: 10.1021/acs.langmuir.5b01354. Copyright (2015) American Chemical Society.

By harvesting both electrons and photons from a liquid drop that is illuminated by X-rays, researchers have developed a new multimodal approach for understanding the redox speciation of targeted metal cations (denoted as M) at the surface and in the bulk of liquid drops (Bera et al. 2015). The initial results for a selection of trivalent metal cations reveal an unexpected polynuclear metal speciation at the surface of the drop; whereas the typical mononuclear speciation expected of an aquated metal cation is found in the bulk interior. This new characterization technique provides a new approach for understanding molecular reactions of solvent extraction systems for the separation of metal ions from aqueous media (Bera and Antonio 2015).

Design and Synthesize Tailored Materials for Improved Separations

The development of new separations materials is critical for efficient processing of tank wastes. Designing materials that can respond favorably to large doses of ionizing radiation would significantly benefit the processing of high-level radioactive wastes. Design approaches must also consider materials performance lifetimes and recyclability at extreme conditions. Highly selective separations approaches can be designed using materials at the molecular- and supramolecular-length scales via chelation. Also, computational approaches can be used to design highly specific supramolecular structures, as demonstrated for the CSSX chelator currently in use at the Savannah River Site.

In addition to developing new materials with enhanced selectivity, fundamental approaches are needed for optimizing the properties of extractive systems to allow process scale up.

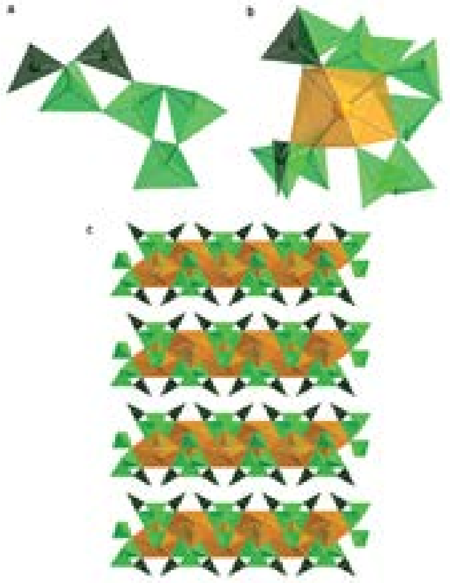


Figure 1. Three (a, b, c) graphical representations of the molecular and crystal structures of a californium(III) borate, Cf[$B_6O_8(OH)_5$]. Actinide borate structures such as these may be used to design new generations of materials for separations and waste forms. With a broader fundamental understanding of their behavior, materials properties such as porosities and ion exchange capacities might be tuned to match specific large-scale processing needs. Reprinted by permission from Macmillan Publishers Ltd: *Nature Chemistry* (Polinski et al. 2014). Copyright 2014.

For new extractants to be process-compatible, they must be resistant to third-phase formation. They must also be either resistant to radiolytic degradation, or preferably, they should exploit changes induced by ionizing radiation. Moreover, new nanomaterials can be employed for sequestration and separations processes. For example, graphene shows remarkable resistance towards radiolytic damage and can also be tailored into nanoporous materials that can separate metal ions, as already demonstrated for water desalination (Surwade et al. 2015) and for selective alkali metal cation binding (Guo et al. 2014). Furthermore, recent progress in actinide borate chemistry (Wang et al. 2011), particularly with regard to their porosity and anion exchange capacities, could lead to the development of high-performance separations and identification of solubility-limited waste forms (Figure 1). A significant advantage of nanoscale materials is that they offer prospects for rational and deliberate designs to provide highly efficient separations. For example, high surface-area materials can be designed to provide specific, uniform pore sizes or can be chemically modified to target specific molecular interactions that can enhance selectivity. To take full advantage of nanoscale materials for separations, a fundamental understanding is required of chemical interactions at the surface of the solid-state separations media and actinide and lanthanide complexes. In summary, advances in fundamental chemistry of interfacial interactions in radiation environments will have a tremendous impact on advancing separations technologies for the EM mission and many other applications important to DOE's energy mission.

Understand Electron-, Ion-, and Radical-Driven Phenomena in Bulk and Interfaces

Redox phenomena that are driven by electron, ion, and radical reactions play important roles in the chemistry of many of the longer lived radionuclides in high-level radioactive wastes. Ionizing radiation produces an avalanche of secondary particles. The most important particles are low-energy electrons, solvated electrons, neutral radicals, radical ions, alpha and beta particles, neutrons, and gamma radiation.

These particles can initiate a cascade of secondary electrons. These secondary electrons can drive unexpected chemical speciation and reactivity including corrosion. The radiolysis reactions shown in Figure 2 rely on water, which is limited in the tank waste systems. The ability to identify the oxidants and reductants, and anticipate or control their impact on the reactivity of the molecular species in the waste streams, is quite limited. Yet this is pivotal knowledge for developing a thorough and predictive understanding of basic chemical phenomena involving absorption, solvation, complexation, exchange, electron transfer, and hydrolysis behaviors, all of which comprise an essential foundation for safe and cost-effective processing of high-level wastes.

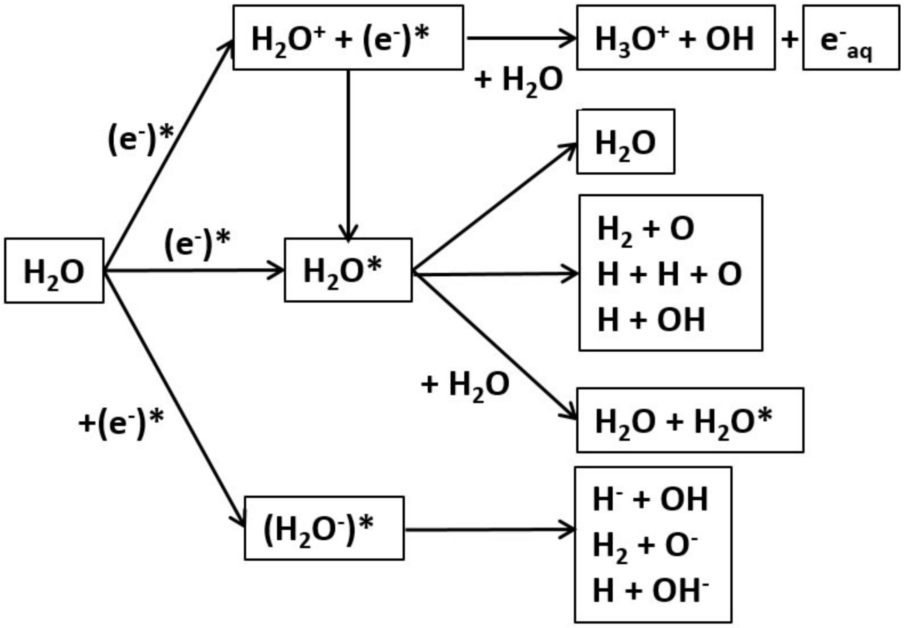


Figure 2. Key processes in the decomposition of water by ionizing radiation showing neutral, ionic, and radial products with various oxidizing and reducing powers. Reprinted with permission from Garrett et al. (2005). Copyright 2005, American Chemical Society.

Little is known about the role of ionizing radiation on the chemical and physical behavior of nanoparticles, colloids, and ultrafine precipitates. Some evidence exists in the literature to suggest that nanoparticles smaller than the mean distance that charge carriers can travel (typically < 100 nm) may enhance the effects of radiation-induced chemistry and production of radiolysis products. In the case of water radiation chemistry, these phenomena are particularly prevalent for metal oxides, such as ZrO_2, that have band gaps of approximately 5 eV and larger. This band-gap energy is nearly resonant with dissociative states of the adsorbed water. Previous work using gamma rays (LaVerne 2005; Petrik et al. 2001) and ultraviolet/vacuum ultraviolet photons (Poston et al. 2014) demonstrate the importance of the chemical identity and phase of the particles in the radiation production of molecular hydrogen during water radiolysis. Combining state-of-the-art experimental and computational approaches could elucidate, for the first time, the role of chemical entities that range from simple aquated ions (angstrom scale) to molecular coordination compounds (nanometer scale), and even macromolecular grains (micron-scale colloidal systems).

Finally, details about the transuranic elements in the inhomogeneous, chemically diverse tank media are generally sparse. Building a foundation for a thorough understanding of redox speciation in aqueous systems of relevance to tank chemistry is a challenging endeavor given the complicating effects such as radiolysis, hydrolysis, disproportionation, oligomerization, precipitation, and competitive binding effects. However, such basic knowledge is essential for designing processing schemes to transform the waste streams into waste forms. Knowledge that is currently lacking includes mechanisms of the relevant solution redox speciation and their influence on the interfacial electrochemical equilibria in such environments, particularly those in which there are strong ionizing radiation fields.

CHARACTERIZATION AND CONTAINMENT: TWO SIDES OF THE SAME COIN

Approximately 200 million liters of radioactive waste are stored in 177 large underground tanks at the Hanford Site in Washington State and approximately 130 million liters in 45 tanks at the Savannah River Site in South Carolina. The wastes, which are now decades old, are highly radioactive, extremely caustic, and contain very high concentrations of electrolytes and precipitated materials, along with radioactive fission products and actinide elements. Additional species include nitrate, nitrite, hydroxide, carbonate, and phosphate ions. While it is possible to list the elements involved, the dynamic nature of the species in the waste continues to bring surprises. For example, the leak in a Hanford Site double-shell tank (Engeman et al. 2012) was attributed to corrosion that should have been inhibited by nitrite and hydroxide ions; nonetheless, it occurred.

The wastes in these tanks require processing to stabilize and contain them in waste forms that must perform for millennia. Designing effective waste forms requires matching the chemistry of the output from the waste processing to the chemistry of the waste form. Given the complexity and evolving nature of the wastes it is a natural but shortsighted tendency to make simple assumptions when devising approaches for processing and stabilizing wastes. However, the complex, dynamic nature of these wastes demands that the numerous components and processes that occur in the tanks be fully understood. Armed with this information, efficient and cost-effective processes can be developed. Processing and stabilizing the wastes requires an intimate connection between the science and engineering involved in characterizing the waste, retrieving it, separating or processing it, and converting it into its final form. Decisions made at each step—whether it is adding water to remove sludge or adding specific chemicals to separate out troubling elements—can significantly alter the waste stream that feeds into stabilization.

Conclusions

According to the current waste processing plans, EM must remove about 300 million liters of highly radioactive materials from underground tanks at the Savannah River and Hanford Sites (see Appendix A), which will result in the generation of nearly 1,100 million liters (Certa et al. 2011) of waste to be processed into waste forms at existing or new facilities. The wastes in these tanks comprise an extraordinarily complex mixture of chemical components under extreme conditions. The difficulties associated with characterizing the materials in the tanks compound issues associated with developing efficient and selective separations processes that are critical for preparing these wastes for disposal. To address these challenges, development of new characterization approaches and generation of new processing and separations concepts are needed. Formulation of these new concepts requires fundamental understanding of the relevant chemical and physical phenomena across broad spatial scales, from atomic to mesoscale. Current knowledge gaps that impede development of new separations approaches are daunting. The gaps include a lack of understanding of the entropic role of long-scale, organic-phase structuring in metal ion partitioning and a lack of knowledge of the use and/or management of rare oxidation states due to placing the separations system under kinetic control. Armed with this fundamental knowledge, wholly new processing schemes can be designed. Recent advances in nanoscience are particularly exciting because they offer the potential to tailor materials characteristics and functionalities to revolutionize both the efficiency and selectivity of separations processes. Further, it may be possible to develop separations systems that adjust to the heterogeneous system and other conditions presented to it, instead of today's concept of a static separations system. In summary, the development of a new generation of processing and separations systems requires fundamental understanding of the speciation and reactivity that occur in radiation environments and conditions of high alkalinity and concentrated electrolytes.

References

Bera MK, G Luo, ML Schlossman, L Soderholm, S Lee, and MR Antonio. 2015. "Erbium(III) Coordination at the Surface of an Aqueous Electrolyte." *Journal of Physical Chemistry B* 119(28): 8734–8745. DOI: 10.1021/acs.jpcb.5b02958.

Bera MK and MR Antonio. 2015. "Polynuclear Speciation of Trivalent Cations Near the Surface of an Electrolyte Solution." *Langmuir* 31: 5432–5439. DOI: 10.1021/acs.langmuir.5b01354.

Bu W, H Yu, G Luo, MK Bera, B Hou, B Lin, M Meron, I Kuzmenko, MR Antonio, L Soderholm, and ML Schlossman. 2014. "Observation of a Rare Earth Ion-Extractant Complex Arrested at the Oil-Water Interface during Solvent Extraction." *Journal of Physical Chemistry B* 118(36): 10662–10674. DOI: 10.1021/jp505661e.

Certa PJ, PA Empey, and MN Wells. 2011. *River Protection Project System Plan.* ORP-11242, Rev. 6, US Department of Energy Office of River Protection, Richland, Washington. http://www.hanford.gov/files.cfm/ORP-11242_REV_6_-_%5B1110050954%5D.pdf.

Engeman JK, CL Girardot, DG Harlow, and CL Rosenkrance. 2012. *Tank 241-AY-102 Leak Assessment Report.* RPP-ASMT-53793, Washington River Protection Solutions, Richland, Washington.

Garrett BC, DA Dixon, DM Camaioni, DM Chipman, MA Johnson, CD Jonah, GA Kimmel, JH Miller, TN Rescigno, PJ Rossky, SS Xantheas, SD Colson, AH Laufer, D Ray, PF Barbara, DM Bartels, KH Becker, KH Bowen, Jr., SE Bradforth, I Carmichael, JV Coe, LR Corrales, JP Cowin, M Dupuis, KB Eisenthal, JA Franz, MS Gutowski, KD Jordan, BD Kay, JA LaVerne, SV Lymar, TE Madey, CW McCurdy, D Meisel, S Mukamel, AR Nilsson, TM Orlando, NG Petrik, SM Pimblott, JR Rustad, GK Schenter, SJ Singer, A Tokmakoff, L-S Wang, C Wittig, and TS Zwier. 2005. "Role of Water in Electron-Initiated Processes and Radical Chemistry: Issues and Scientific Advances." *Chemical Reviews* 105(1): 355–390. DOI: 10.1021/cr030453x.

Guo J, J Lee, CI Contescu, NC Gallego, ST Pantelides, SJ Pennycook, BA Moyer, and MF Chisholm. 2014. "Crown Ethers in Graphene." *Nature Communications* 5: 5389. DOI: 10.1038/ncomms6389.

Knope KE and L Soderholm. 2013. "Solution and Solid-State Structural Chemistry of Actinide Hydrates and Their Hydrolysis and Condensation Products." *Chemical Reviews* 113(2): 944–994. DOI: 10.1021/cr300212f.

LaVerne JA. 2005. “H_2 Formation from the Radiolysis of Liquid Water with Zirconia.” *Journal of Physical Chemistry B* 109(12): 5395−5397. DOI: 10.1021/jp044167g.

Lukens WW, DK Shuh, NC Schroeder, and KR Ashley. 2004. “Identification of the Non-Pertechnetate Species in Hanford Waste Tanks, Tc(I)-Carbonyl Complexes.” *Environmental Science & Technology* 38(1): 229–233. DOI: 10.1021/es034318d.

Petrik NG, AB Alexandrov, and AI Vall. 2001. “Interfacial Energy Transfer During Gamma Radiolysis of Water on the Surface of ZrO_2, and some other Oxides.” *Journal of Physical Chemistry B* 105: 5935−5944. DOI: 10.1021/jp004440o.

Polinski MJ, EB Garner, R Maurice, N Planas, JT Stritzinger, TG Parker, JN Cross, TD Green, EV Alekseev, SM Van Cleve, W Depmeier, L Gagliardi, M Shatruk, KL Knappenberger, G Liu, S Skanthakumar, L Soderholm, DA Dixon, and TE Albrecht-Schmitt. 2014. “Unusual Structure, Bonding and Properties in a Californium Borate.*” Nature Chemistry* 6: 387–392. DOI: 10.1038/nchem.1896.

Poston MJ, AB Aleksandrov, DE Sabo, ZJ Zhang, and TM Orlando. 2014. “UV Photon-Induced Water Decomposition on Zirconia Nanoparticles.” *Journal of Physical Chemistry C* 118: 12789–12795. DOI: 10.1021/jp501135r.

Pourbaix M. 1966. *Atlas of Electrochemical Equilibria in Aqueous Solutions*. National Association of Corrosion, 2nd edition. CEBELCOR: Brussels, Belgium.

Rimando RV, Jr. 2015. “Enabling Cleanup Innovation.” *Pre-Workshop Webinar: Basic Research Needs for Environmental Management*. June 25, 2015, pp. 12.

Russel RL, RA Peterson, HD Smith, DE Rinehart, PM Aker, and EC Buck. 2009. *Development and Characterization of Boehmite Component Simulant.* PNNL-18176, Rev. 1, Pacific Northwest National Laboratory, Richland, Washington.

Scoppola E, E Watkins, G Li Destri, L Porcar, RA Campbell, O Konovalov, G Fragneto, and O Diat. 2015. “Structure of a Liquid/Liquid Interface During Solvent Extraction Combining X-Ray and Neutron Reflectivity Measurements.” *Physical Chemistry Chemical Physics* 17: 15093–15097.

Serne and Rapko. 2014. *Technetium Inventory, Distribution, and Specification in Hanford Tanks.* PNNL-23319, Pacific Northwest National Laboratory, Richland, Washington.

SRNL – Savannah River National Laboratory. 2015. *Annual Report, Spring 2015. Identifying Cost Effective Tank Waste Characterization Approaches*. SRNL-STI-2015-00144, Savannah River National Laboratory, Aiken, South Carolina.

Surwade SP, SN Smirnov, IV Vlassiouk, RR Unocic, GM Veith, S Dai, and SM Mahurin. 2015. “Water Desalination using Nanoporous Single-Layer Graphene.” *Nature Nanotechnology* 10: 459–464. DOI: 10.1038/nnano.2015.37.

Wang S, EV Alekseev, W Depmeier, and TE Albrecht-Schmitt. 2011. “Recent Progress in Actinide Borate Chemistry.” *Chemical Communications* 47: 10874–10885. DOI: 10.1039/C1CC14023J.

PANEL 2: WASTE FORMS

Abstract

Waste forms employed for geologic disposal of EM's radioactive wastes must be stable for millennia to prevent release of hazardous materials to the environment. These stringent requirements demand revolutionary concepts be developed to address current technology gaps and yield effective materials for safe, long-term waste disposal, or EM's mission will be at significant risk. Developing new concepts will require a fundamental understanding of both the structure of the waste forms and the mechanisms involved in their degradation, which can be enabled by state-of-the-art characterization techniques. New computational tools are needed both to design new materials and predict performance of these materials over broad timescales. Similar advances in fundamental knowledge are needed to design and assure the performance of new structural materials used in both waste processing and disposal. The enormous challenges defined by current technology gaps for waste forms and structural materials will require multidisciplinary teams to assess the full range of issues that ultimately impact the performance of these materials for meeting EM's mission requirements.

Introduction

Past DOE nuclear materials production activities resulted in a legacy of radioactive wastes that are stored at locations across the United States. These wastes take many forms: solid and liquid; high and low radioactivity; and short and long half-lives. Regardless of their form or characteristics, materials play a critical role in storing, processing, and ultimately disposing of these wastes. Highly radioactive liquid wastes, which contain caustic solutions of inorganic and organic materials, must be stabilized into waste forms that will sequester the contaminants for millennia. Before producing the waste form, the wastes are stored in tanks. Special attention must be paid to the stability and integrity of materials used for the waste forms, storage tanks, and processing lines due to extremes in radiation and chemical reactivity. In addition to these highly radioactive wastes, DOE-owned spent nuclear fuels are an additional waste that will be disposed of directly. In this case, the spent fuel serves as the waste form and includes the original fuel assemblies that have been exposed to large doses of radiation during their use. The spent nuclear fuel waste package contains significant quantities of radioactive fission products and actinides from irradiation; they have also experienced extreme temperature changes.

Ultimately, the waste must be prepared for geologic disposal to minimize their impact on human health and the environment. For liquid wastes, the radioactive and/or hazardous constituents are typically processed and immobilized in vitreous (glass) or cementitious matrices. The vitrified wastes will be disposed of in a repository where the waste form itself can serve as a barrier to releasing radionuclides. However, the waste form barriers are supplemented by either natural barriers, such as the host rock formation in which the repository is constructed, or engineered barriers, such as canisters, casks, overpacks, or drip shields. For low-level waste, the waste form itself, which can be vitreous, cementitious, or composed of other materials, will often be used as the primary barrier to environmental release. A primer on waste form types, retention mechanisms, durability, and loading, along with examples, is provided in Appendix C.

Degradation of any of the materials used for the waste forms, tanks, processing vessels, piping, cladding, and associated barriers can lead to unexpected release of contaminants to the environment; thus, the long-term (hundreds to thousands of years) integrity of these materials is of utmost importance. However, today's materials do not meet the full range of requirements needed for safe and effective long-term waste storage, handling, and disposal. This requires development of new materials that are resilient in the harsh environments encountered in these applications to ensure the contaminants are properly sequestered for centuries to come. Recent advances in nanoscale science, characterization, and computation have the potential, for the first time, to enable the fundamental understanding of the myriad chemical and physical processes associated with degradation of waste storage materials. Improved understanding of these highly coupled processes will significantly improve development of new materials for radioactive waste storage, processing, and long-term disposal as well as development of highly reliable models for stability of these materials.

Fundamental Challenges and Research Opportunities

Advancing Materials for Waste Forms

Advances in materials are needed to ensure the long-term stability and safety of waste storage, including revolutionary concepts in glasses and cementitious materials, as well as wholly new storage materials concepts. Glasses are solid-state materials that have a topologically disordered internal structure made of a three-dimensional network of interconnected structural blocks. Because of the disordered arrangement of structural blocks, glasses can accommodate the wide range of elements that are present in the wastes, allowing them to be retained within the glass structure. In the past, glass was only considered to exhibit short-range order; however, analyses of complex glasses using high-resolution analytical tools have revealed that medium-range structural features may also exist (Caurant et al. 2009). An enhanced understanding of both short- and medium-range order and the effects on properties and performance of glass waste forms is vitally needed to develop improved glass materials.

Waste loading in glass is a key parameter that impacts cost and efficiency of EM’s vitrification facilities as well as the long-term stability of these waste forms. Currently, formation of these highly complex vitreous materials is poorly understood. Crystallization within the glass, formation of secondary phases (for example, salt formation) and phase separations all constrain waste loading and long-term durability (Kim et al. 2011). The structures of these materials need to be understood from the nano- to mesoscales to develop glass forms that can increase waste loading; even small gains in waste loading can yield dramatic savings in operating and disposal costs. Further, this information could be coupled with processing properties during glass formation in the melter (viscosity, liquidus temperature, electrical conductivity, etc.) to provide input for computational modeling and establish optimum conditions to form the desired glass structures.

Thermochemical representations of complex melts, glasses, and crystalline phases are important for understanding the development and behavior of nuclear waste forms, including determining and predicting melt temperatures, precipitation temperatures, viscosity, chemical activities and vapor pressures, phase separation, glass- and crystalline-phase compositions, and stability and durability. While models do exist for relatively simple oxide systems, they do not exist for the highly complex materials represented by various waste form materials. For example, first principles or ab initio methods break down when a substantial number of species need to be considered, and high-z systems (for example, lanthanides or actinides) present substantial bottlenecks to modeling these complex systems.

Fundamental approaches must be developed to generate thermochemical models and values for systems of interest. For example, these approaches could be applied to multielement spinels or nepheline ($Na_3KAl_4Si_4O_{16}$) crystalline phases (see Figure 3), which are problematic with regard to glass melter operation and waste form stability, respectively.

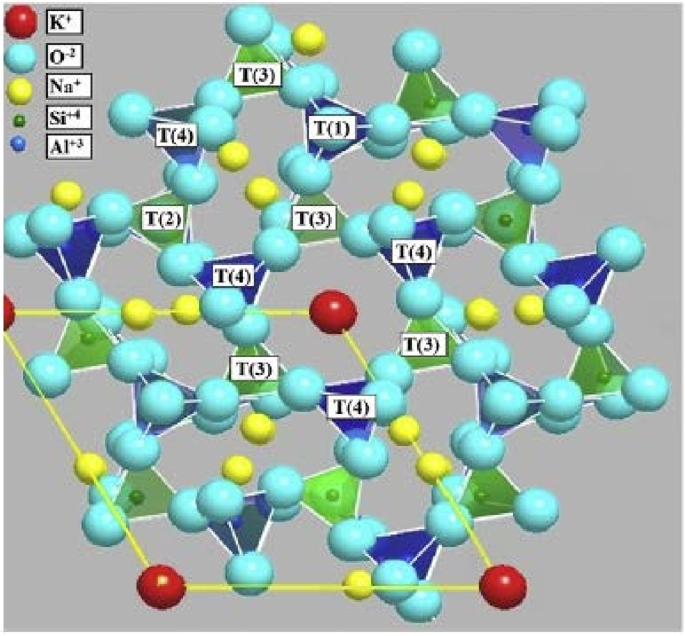


Figure 3. Structure of hexagonal nepheline according to Hahn and Buerger (1954). View along c-axis of the P63 hexagonal nepheline structure showing layer of framework tetrahedra that point alternately up and down and consist of nominally alternating silicon and aluminum atoms. Reprinted from John McCloy et al. (2015). Copyright 2015, with permission from Elsevier.

Knowledge and ultimately control of the chemistry and structure of cementitious waste forms is important for the efficient processing and long-term performance for disposal of low-activity wastes. A thorough understanding of the mechanisms that bind the radionuclides in the waste form matrix and the mechanisms that impact the evolution of the waste form properties as a function of time and changing conditions in the disposal environment is essential. In particular, understanding of the chemical and structural mechanisms controlling transport through these multiphase, porous materials with features ranging from the nano- to micrometer scale is required. In addition to improving waste form processing and performance, this insight could expand the utility of these low-cost waste forms to work with wastes that contain higher levels of radioactivity.

Beyond these conventional wastes forms, a new generation of materials could be designed to enhance waste form performance. For example, secondary structures with materials property enhancements have been developed via colloidal synthesis to control particle size and composition at the nanoscale (Lu and Yin 2012). Such materials-by-design approaches could be exploited to develop advanced waste forms with tailored loading and durability properties. Further, these tailored waste forms could be applied to radionuclides that are not effectively managed by current bulk waste processing. Examples include ^{131}I, ^{135}Cs, and ^{99}Tc, which are volatile during processing and ineffectively incorporated into glass waste forms.

Understanding Materials Degradation in Highly Complex Environments

Knowing how materials perform when exposed to harsh environments—environments that push the material away from equilibrium—is a Grand Challenge of the materials science community (BESAC 2007, 2015). In particular, the radiation damage that accompanies nuclear materials leads to defects that diffuse and agglomerate, causing macroscopic changes in the properties of the material. Thus, events that occur on the picosecond timescale and atomic length scale result in changes on the macroscale that can take years or decades to manifest. An important example of this is the embrittlement of reactor pressure vessels that occurs because of nanoscopic clustering of alloying elements (Pareige et al. 1997).

In materials of interest to EM, a further complication is the concurrent chemical evolution of the material. As radioactive species decay, their chemical identities change, and radiation-induced damage can also occur in crystalline materials (see sidebar). Thus, in many contexts it is important to understand not only how the damage processes alter the microstructure of the material, but also how the concurrent changes in chemistry couple with those defect fluxes to possibly alter the phase structure of the material.

TANK AND INFRASTRUCTURE STRUCTURAL INTEGRITY

A Cold War legacy nuclear materials management challenge is maintaining the structural integrity of the aging infrastructure for the storage and transfer of high-level waste stored in more than 200 large underground tanks at various DOE sites.

The tanks are fabricated from welded and stress-relieved steel (see Appendix A). Hot nitrate solutions are known to attack steel, resulting in pit and crack formation. This attack can be inhibited by nitrite and hydroxide ions; thus, this corrosion process is currently controlled by adding inhibitors when needed. However, steel tanks have failed over the years and even recently, resulting in leaks into the environment or the annular space of double-shelled tanks.

A fundamental understanding of the mechanisms of corrosion and development of new approaches to inhibit corrosion in tank environments is crucial for continued safe operation of the tanks, as well as for other materials used in waste processing and long-term waste disposal.

Understanding these effects requires an integrated experimental and theoretical approach, which is now becoming possible with advanced computational and characterization tools. While insight into these problems has been obtained, particularly how radiation induces redistribution of chemical species in complex alloys—radiation-induced segregation (Murty and Charit 2008)—coupling this structural information with evolving chemistry has received little attention. Importantly, while one might be able to achieve a steady-state microstructure if the chemistry is constant; once it begins to evolve with time, a true steady state cannot be reached as the equilibrium of the system is evolving with time (see sidebar).

RADIATION EFFECTS ARE COUPLED WITH CHEMISTRY

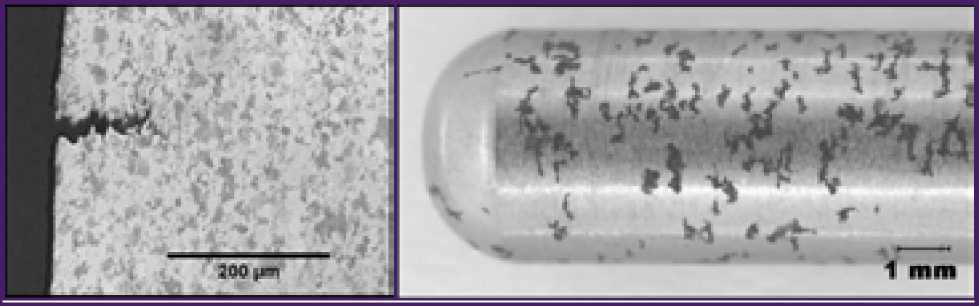
During neutron irradiation of uranium, fission transmutes the uranium atoms into other atoms of other elements and their isotopes, the yields of which depend in part on neutron energy and neutron capture cross sections. The isotopes of ^{137}Cs and ^{90}Sr are produced in large quantities and make up the majority of the radionuclide inventory that requires disposal as high-level radioactive waste. Both isotopes are beta decay processes with half-lives of approximately 30 years; ^{137}Cs decays to isotopes of barium while ^{90}Sr decays to isotopes of yttrium. The physical damage mechanisms from beta decay may be minor, as direct interaction with lattice by the associated beta particles is very weak; however, low-energy electrons and electronic excitations can occur that dramatically alter the chemical behavior of the material. While these physical damage processes are occurring, thereby altering the defect structure of the material, the chemistry is also evolving, but little is known about how the physical and chemical changes couple together. In addition, the rate at which these changes occur are controlled by the half-life of the isotopes; predicting this behavior over many radioactive half-lives (perhaps hundreds of years) is very challenging. Radiation effects are not unique to the wastes, as they also occur in nuclear fuel and structural components of a reactor during irradiation and transmutation. In these cases, however, there is significantly more physical damage as a consequence of ballistic events from bombardment of neutrons, alpha particles, and other swift heavy ions.

Corrosion is another means through which waste forms and waste containment materials degrade (see sidebar). The environments of radioactive wastes are far more complex and reactive than those found in more typical materials applications. In fact, exposure to high concentrations of highly reactive anions (for example, nitrate, nitrite, carbonate, and phosphate), high radiation fluxes and temperatures, mixed phases, and often dynamic or flowing solutions make understanding these corrosive degradation processes especially challenging. For example, radiolytic contributions to processes involving absorption, solvation, complexation, exchange, electron transfer, and hydrolysis and their impact on corrosion remain mostly unstudied. A further complication in waste processing is flow-accelerated corrosion, which results from flowing particulate-laden fluids across surfaces with protective films, leading to corrosion.

Metals in fuel-cladding materials, waste tanks, fuel casks, special nuclear material storage containers, and process vessels are all subject to corrosion that could lead to failure. Understanding the highly coupled or synergistic effects responsible for corrosive degradation in metallic systems is needed to design a new generation of materials for these applications. In the case of the carbon-steel, high-level waste tanks currently used, empirical relationships have provided the bases to control the tank chemistry to minimize corrosion. However, the effects of all physical and chemical processes occurring in the tanks that contribute to corrosion processes are simply not known. This will require a detailed understanding of processes that occur at the interface of the metal with the tank waste, process solutions, and even groundwater. Elucidation of interfacial chemical and physical processes occurring in these boundary regions would lead to development of new classes of materials that could withstand the highly demanding environments of radioactive waste solutions. These new materials could also find uses in energy applications where service in extreme environments is required.

CORROSION: DEGRADATION OF MATERIALS IN EXTREME ENVIRONMENTS

In general, corrosion is a primary basis of materials degradation, causing trillions of dollars of damage annually worldwide. Corrosion may be defined simply as the environmental degradation of materials. This degradation occurs by chemical means whereas purely mechanical degradation is not part of corrosion. Most people think of corrosion as being metallic degradation, such as rusting steel. However, other materials corrode through environmental degradation, including glasses, ceramics, and polymers. Metallic corrosion can take many forms that look different; uniform corrosion, pitting, crevice corrosion, and environmental cracking. However, the same electrochemical principles underlie all of them. Metal atoms increase oxidation state and release electrons, which are consumed by a reduction reaction, such as the reduction of oxygen or water. The rate of oxidation, or corrosion, is dependent on both the environmental conditions and details of the metal surface. Oxide glasses and ceramics are much more thermodynamically stable than metals and are generally more corrosion resistant. However, they will corrode in sufficiently aggressive environments. This attack is usually not electrochemical in nature.



Different forms of steel corrosion after testing in a tank waste simulant (left to right): environmental cracking, pitting corrosion, and liquid-air interface corrosion (Brossia et al. 2007a and 2007b). Left: Image courtesy of DOE; right: image courtesy of DOE Office of River Protection.

Glass waste forms are thought to degrade by a series of processes, including

- Hydration of the three-dimensional network of interconnected structural blocks, leading to dissolution at the surface of the glass
- Transport of species to and from the reacting glass surface

- Ion exchange within the solid glass
- Precipitation of alteration products that change the system chemistry (Vienna et al. 2013).

The rates of these processes are strongly influenced and coupled through the surface structure and solution chemistry, which are in turn influenced by the reacting glass and by reaction with the near-field materials and precipitation of alteration products (Figure 4). Based on initial models and the evaluation of natural analogs, waste glasses have lifetimes greater than a million years. However, the study of glass corrosion in prototypic conditions is extremely challenging because reaction rates are on the order of 10^{-5} g/m^2/day. New experimental and computational techniques are needed to provide detailed information on the mechanisms responsible for glass corrosion over long timescales.

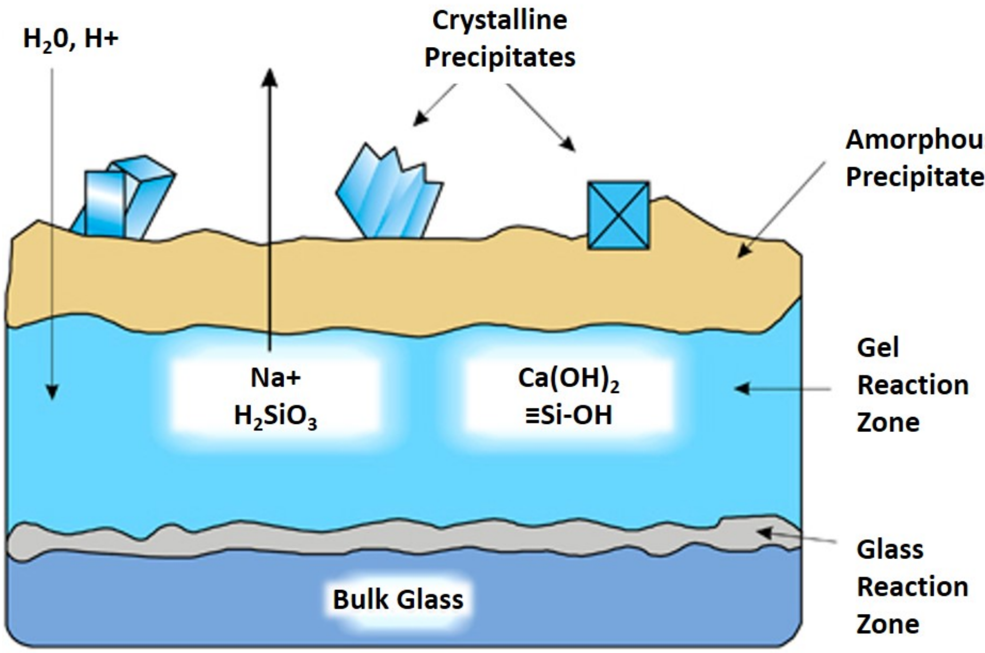


Figure 4. Schematic diagram of glass dissolution mechanisms (ion exchange and matrix dissolution) in aqueous solution, coupled with both hydrated amorphous surface layer formation and crystallization/precipitation from solution. Image courtesy of Carol M. Jantzen (Jantzen et al. 2010).

Cementitious materials used for low-level storage also degrade and affect the transport of highly mobile radionuclides (tritium, residual cesium, strontium, and long-lived isotopes such as technetium, neptunium, iodine, and ^{14}C). Thus, it would be especially valuable to understand and control the various degradation processes to expand the utility of this low-cost waste disposition form. These cementitious materials are difficult to study, however, because they are porous and have multiple phases. As a result, the mechanisms of radionuclide binding in cement are not well understood at present, nor are the chemical and physical mechanisms responsible for transport through these multiphase materials. Further, the reactivity of specific species, such as selective redox-sensitive species including technetium(IV, VII), in these porous materials remains elusive.

Predicting contaminant release from disposal systems using glass or cementitious waste forms is inherently difficult because of the heterogeneous nature—multicomponent, multiphase, nonequilibrium—of the system. Furthermore, short-term test data (months to years) may not fully capture all of the long-term processes that can impact estimates of waste form performance over geologic timescales spanning

10,000 years or more. Therefore, to obtain a thorough understanding of radionuclide release and transport in heterogeneous systems over large timescales and relate observed experimental phenomenon to actual long-term performance, new high-performance computational methodologies are needed. Such information is critical for obtaining a license to place solid radioactive waste in a subsurface disposal facility. This is because the long-term performance of these materials, specifically the release rate of radionuclides into the environment and the associated corrosion or weathering rates of the solid waste form, must be understood to fully assess the impacts of the disposal facility on public health and environmental resources. Thus, a sound scientific basis for determining the long-term release rates of radionuclides from radioactive waste forms must be developed if the performance assessment is to be accepted by regulatory agencies and the public. Another critical need is new analytical techniques that can operate in harsh environments of extreme radiation. In particular, a new generation of sensors is needed to monitor materials in situ to increase the safety and security of stored wastes.

Conclusions

New materials are critically needed for the long-term, safe, and reliable immobilization of radioactive and hazardous waste constituents currently being stored at EM sites. The vast varieties of waste inventory preclude a one-size-fits-all approach for waste stabilization. Therefore, several waste form matrices are required to provide predictable immobilization over many hundreds and even thousands of years. The complexity of the waste form chemistries present extreme scientific challenges in obtaining a fundamental understanding of the myriad processes that can cause deterioration and failure of storage materials. Understanding the inextricably linked chemical and physical processes that occur in the materials across different timescales will require new approaches using high-performance computing to assimilate results from short-term measurements (femtoseconds to many hours) and project the results to hundreds and thousands of years.

References

BESAC – Basic Energy Sciences Advisory Committee. 2007. *Directing Matter and Energy: Five Challenges for Science and the Imagination*. US Department of Energy, Washington, DC.

BESAC – Basic Energy Sciences Advisory Committee. 2015. *Challenges at the Frontier of Matter and Energy: Transformative Opportunities for Discovery Science*. US Department of Energy, Washington, DC.

Brossia C, C Scott, JA Beavers, MPH Brongers, GL Edgemon, H Berman, GS Frankel, L Stock, and B Wiersma. 2007a. "Inhibition of Stress Corrosion Cracking of Carbon Steel Storage Tanks at Hanford." In *CORROSION 2007, March 11-15, Nashville, Tennessee*. Paper 07606. NACE International.

Brossia C, C Scott, and F Gui. 2007b. *Hanford Tanks AY-102 and AP101: Effect of Chemistry and Other Variable on Corrosion and Stress Corrosion Cracking*. RPPT-33284, Rev. 1, Ares Corporation, Richland, Washington.

Caurant D, P Loiseau, O Majerus, V Aubin-Chevaldonnet, I Bardez, and A Quintas. 2009. *Glasses, Glass-Ceramics and Ceramics for Immobilization of Highly Radioactive Nuclear Waste*. Nova Science Publishers, Inc., New York.

Hahn T and MJ Buerger. 1954. "The Detailed Structure of Nepheline, $KNa_3AL_4Si_4O_{16}$." *Zeitschrift für Kristallographie – Crystalline Materials* 106(1–6):308–338. DOI: 10.1524/zkri.1954.106.16.308.

Jantzen CM, KG Brown, and JB Pickett. 2010. "Durable Glass for Thousands of Years." *International Journal of Applied Glass Science* 1(1): 38–62. DOI: 10.1111/j.2041-1294.2010.00007.x.

Kim D, MJ Schweiger, CP Rodriguez, WC Lepry, JB Lang, JV Crum, JD Vienna, FC Johnson, JC Marra, and DK Peeler. 2011. *Formulation and Characterization of Waste Glasses with Varying Processing Temperature*. PNNL-20774, EMSP-RPT-009, Pacific Northwest National Laboratory, Richland, Washington.

Lu Z and Y Yin. 2012. "Colloidal Nanoparticle Clusters: Functional Materials by Design." *Chemical Society Reviews* 41(21): 6874–6887. DOI: 10.1039/C2CS35197H.

McCloy J, N Washton, P Gassman, J Marcial, J Weaver, and R Kukkadapu. 2015. "Nepheline Crystallization in Boron-Rich Alumino-Silicate Glasses as Investigated by Multi-Nuclear NMR, Raman and Mössbauer Spectroscopies." *Journal of Non-Crystalline Solids* 409: 149–165. DOI: 10.1016/j.jnoncrysol.2014.11.013.

Murty KL and I Charit. 2008. "Structural Materials for Gen-IV Nuclear Reactors: Challenges and Opportunities." *Nuclear Materials* 383(1–2): 189–195. DOI: 10.1016/j.jnucmat.2008.08.044.

Pareige P, RE Stoller, KF Russell, and MK Miller. 1997. "Atom Probe Characterization of the Microstructure of Nuclear Pressure Vessel Surveillance Materials after Neutron Irradiation and after Annealing Treatments." *Journal of Nuclear Materials* 249(2–3): 165–174. DOI: 10.1016/S0022-3115(97)00215-8.

Vienna JD, JV Ryan, S Gin, and Y Inagaki. 2013. "Current Understanding and Remaining Challenges in Modeling Long-Term Degradation of Borosilicate Nuclear Waste Glasses." *International Journal of Applied Glass Science* 4(4): 283–294. DOI: 10.1111/ijag.12050.

PANEL 3: CONTAMINANT FATE AND TRANSPORT IN GEOLOGICAL ENVIRONMENTS

Abstract

Legacy contamination in the environment threatens the areas surrounding EM waste sites; this contamination includes soils, vadose zone, groundwater, and hyporheic and riverine subsystems. Understanding and predicting contaminant behavior in these subsurface systems are required for developing efficient and cost-effective remediation. Currently, these subsystems are poorly understood because of their heterogeneity and inaccessibility. New approaches are critically needed to characterize and monitor the components of these systems, which include interfaces of fluids and solids; numerous inorganic, organic, and mineralogical species; and communities of microorganisms. These various components contribute to astonishingly complex systems that must be understood to predict their behavior over broad spatial and temporal scales. Armed with a stronger scientific basis, revolutionary approaches for environmental remediation could be devised, including controlling the transport and transformation of species via biogeochemical processes to enhance cleanup processes.

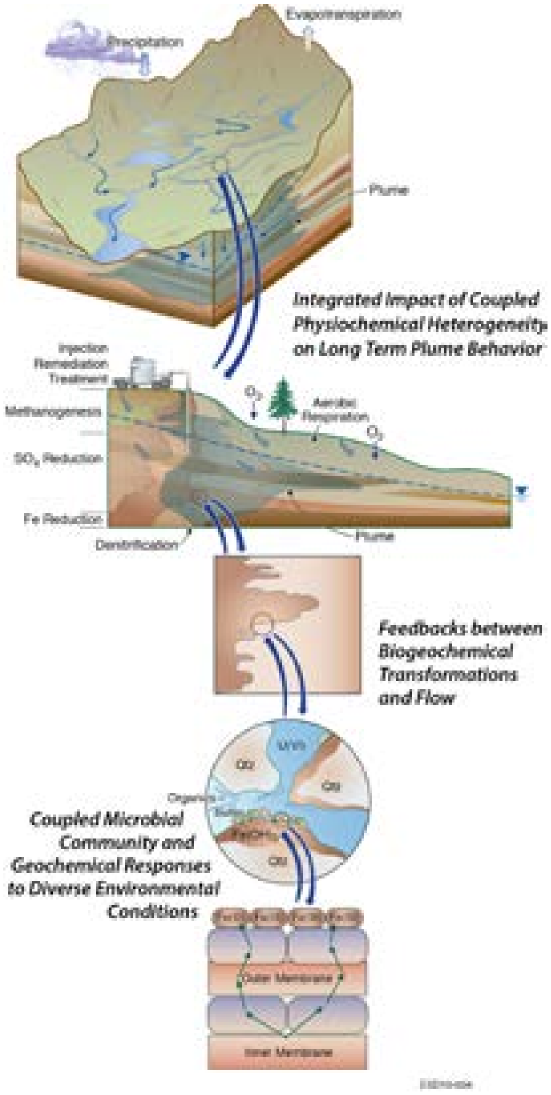


Figure 5. Contaminant fate and transport in geological environments is governed by coupled hydrological, physical, geochemical, and microbiological properties and processes that occur over a wide range of spatial and temporal scales. Image courtesy of Susan Hubbard (Hubbard and Linde 2011), Lawrence Berkeley National Laboratory. Copyright 2011, Elsevier Ltd. All rights reserved.

Introduction

The Earth's subsurface serves as a reservoir for much of its fresh water as well as a majority of contaminants from EM legacy nuclear waste sites. As described in Appendix A, DOE manages one of the largest groundwater and soil remediation efforts in the world. The inventory at the sites includes 6.5 trillion liters of contaminated groundwater, an amount equal to about four times the daily US water consumption, and 40 million cubic meters of soil and debris contaminated with radionuclides, metals, and organic chemicals. Remediation of legacy waste sites requires a predictive understanding of subsurface processes and properties that influence the fate and transport of these contaminants as well as a scientific underpinning to guide the development of next-generation remediation approaches that will be both effective and sustainable over decadal-to-century timeframes.

Developing a predictive understanding of subsurface flow and transport is hindered by the multiscale complexity of the subsurface (Figure 5)—a dynamic system that includes heterogeneities at all scales. The far-from-equilibrium, non-ideal subsurface environment, which encompasses the vadose and saturated zones, is actively linked to surface waters, the soil-plant system, and the atmosphere. The subsurface mineral matrix and associated pore fluid is populated by diverse suites of microorganisms and metazoans that mediate biogeochemical cycles of both nutrient and contaminant elements. Mineral, water-dissolved, and biologic constituents interact within the structured geological subsurface in complex ways—over length scales of microns to kilometers and timescales ranging from picoseconds to millennia and longer.

Over the last several years, DOE Office of Science workshops have identified fundamental gaps that limit predictive understanding of subsurface flow and transport. Understanding the fundamental coupling of hydrological, geochemical, and biological processes and its control on how the larger system functions has been identified as a Grand Challenge for subsurface flow and transport (BERAC 2010; BESAC 2015; DOE 2010). Examples of select fundamental research needs include quantifying dynamics of interfaces and molecular and nanoscale controls on macroscopic physical, geochemical, and biological processes (BESAC 2007, 2015). Fundamental advances are needed to understand rate-controlled reactions in perturbed environments and enable simulation of coupled processes and scale transitions occurring in hierarchical geological systems—from native scales where processes occur to watershed or larger scales where systems are managed, and as systems are perturbed through natural and anthropogenic events. Approaches are needed to enable real-time monitoring of these perturbations, at spatial scales relevant to the individual process as well as the contaminated system response.

Fundamental Challenges and Research Opportunities

Several fundamental basic science challenges exist that, if met, have the potential to lead to transformative approaches to quantify, predict, and control the fate and transport of environmentally hazardous contaminants in the subsurface. These science challenges are encompassed by the following five key areas:

- Radionuclide speciation and transformations
- Transient perturbations
- Low-permeability domains
- Four-dimensional sensing of the subsurface
- Predicting properties of multiscale systems.

Speciation and Biogeochemical Transformations of Radionuclides in the Environment

Because of its ubiquity, mobility, and strong solvation properties, liquid water profoundly affects subsurface contaminants, redistributing it into plumes, surface waters, and difficult-to-remediate low-permeability sediments (for example, soil saprolite). Inorganic and organic solids act in concert with water by supplying and retaining contaminants, often for decades or hundreds of years. Microbes and reactive solutes such as oxygen, nitrate, and organic compounds further modify the contaminant chemical state. Thus, water-solute-microbe-solid interactions control the transport of contaminants in subsurface geologic environments. Conceptualizing and quantifying reaction networks in these multicomponent, multiphase systems (that is, solutes, colloids, particles, and mineral surfaces) are exceptionally challenging activities given that subsurface environments can exhibit extraordinary ranges in chemical gradients of salt loading, pH, and oxidation state. Temperature and pressure can also exhibit lateral and vertical variability. It is not uncommon to observe extraordinary complexity in solid phase composition and structure. Meeting these challenges is essential to providing the fundamental scientific basis that supports quantitative modeling, risk assessment, and compliance strategies. The speciation and reactivity of radionuclides and heavy metals in heterogeneous subsurface environments in extreme near-field and dilute far-field settings are complex and currently insufficiently understood. Risk-driving radionuclides or legacy contaminants (for example, uranium, plutonium, technetium, cesium, strontium, iodine, and nonradionuclides such as chromium, mercury, arsenic, and selenium) exhibit poorly understood chemical and physical forms in biogeochemical environments that evolve over time and space, limiting predictability of their fate and transport.

A rigorous structural, kinetic, and thermodynamic description of the complex chemical pathways connecting molecular-level reactions and macroscopic-scale transport is a fundamental scientific challenge (see sidebar). Recent advances have been made in analytical probes for characterizing aqueous species, volatiles, and complex solids from the nanometer-to-centimeter size range. Coupled with advances in the theory available to calculate the properties of complex mixtures and in the performance of computational platforms available for simulation, scientists have never-before-available tools to fundamentally understand complex Earth materials at an unprecedented level of atomic specificity. One critical research need is to determine the valence, bonding, physical structure, and phase composition and structure of risk-driving radionuclides in complex biogeochemical environments in the form of aqueous solutes, clusters, nanoparticles, sorbates, and incorporated ions in inorganic, organic, and biological materials.

A second important research need is to understand how speciation and conditions that are extreme in their compositional and temporal variability affect reactivity, kinetics of nucleation, redox transformations, and mobility of risk-driving radionuclides. Determination of how metastable species and solids evolve over a range of time and length scales is another significant challenge, because these species can be very long-lived and control their local environments while being thermodynamically unstable.

Research on speciation and biogeochemical transformations of risk-driving radionuclides in the environment will lead to novel, broadly relevant impacts, starting with a quantitative description of inorganic and metallo-organic coordination chemistry of *f*-elements (uranium, plutonium) and weakly solvated ions such as cesium, pertechnetate, selenite, and iodine. New understanding of the effects of high ionic strength and radiation on risk-driving radionuclide forms, stability, reactivity, and mobility will lead to a more quantitative description of the behavior of contaminants in ever-changing natural environments. Fundamental discoveries in this area will also lead to a chemically and physically informed rational design of risk-driving radionuclide remediation and geologic disposal strategies. This insight will lead to improved confidence in understanding natural attenuation processes and the effects of perturbations as well as development of validated computational models that will support improved decision making.

LARGE- AND MICROSCALE INTERACTIONS AND URANIUM'S PERSISTENCE

At DOE's Rifle field site in Colorado, the Colorado River discharge (blue) corresponds with groundwater elevation (red) and groundwater uranium concentrations (green). Increased discharge accompanying late spring snowmelt induces a synchronous rise in groundwater elevations across the Rifle floodplain, which enables oxidation and leaching of uranium-contaminated materials left in place following reclamation activities at the site. This annual coupling sustains uranium delivery to the Rifle aquifer and ensures plume persistence so long as discharge-induced increases in groundwater are sufficient to enable leaching of residual contaminant inventories in the shallow subsurface (Williams et al. 2015).

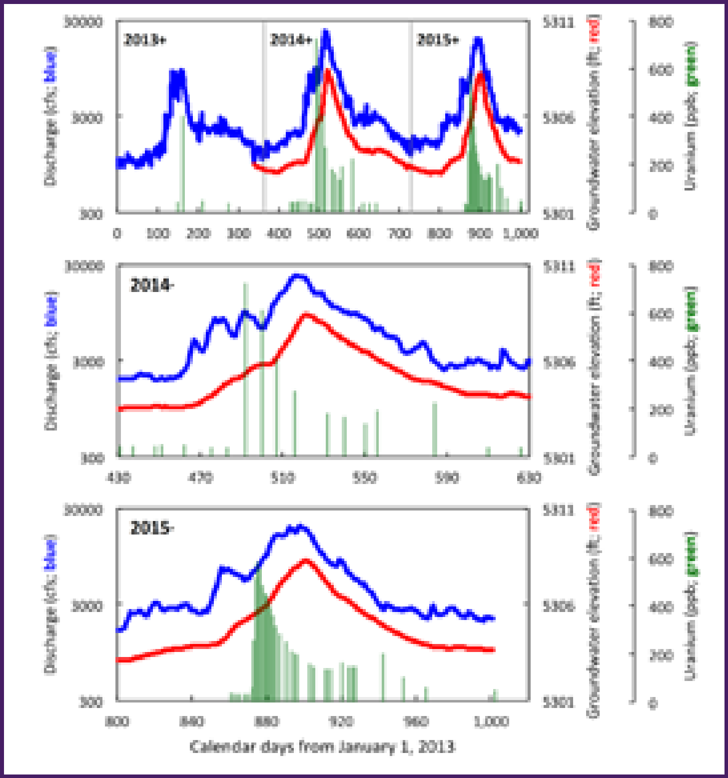


Image courtesy of Kenneth Hurst Williams, Lawrence Berkeley National Laboratory.

Consequences of Transient Perturbations on System Behavior

The capacity to effectively manage remediation activities depends on harnessing multiple physical, geochemical, and biological data into a site-predictive framework; however, the current understanding of subsurface processes often fails to account for how natural or anthropogenic perturbations at local, regional, and global scales will impact the subsurface biogeochemical landscape. This knowledge gap is made even more vital today given that land-use and climate-induced perturbations are already impacting the fate and transport of contaminants in the subsurface.

Transient perturbations can result in elevated biogeochemical activity that is potentially important for contaminant fate and transport. Examples include pulses of increased uranium leaching from near-river sediments during increased river stage (see sidebar). These perturbations can result from natural and anthropogenic events (for example, hurricanes, landslides, fires, and contaminant release) or transient conditions resulting from short-term changes in hydrologic or chemical fluxes and gradients. These perturbations may locally stimulate biogeochemical activity where hydrological flow paths intersect or encounter a substrate containing complementary reactants. These perturbations can potentially lead to beneficial uses such as remediation. For example, episodic dissolved organic carbon input from near-stream soils, which occurs during snowmelt, activates plant and microbial activity, leading to enhanced nitrogen cycling (Pickett and White 1985).

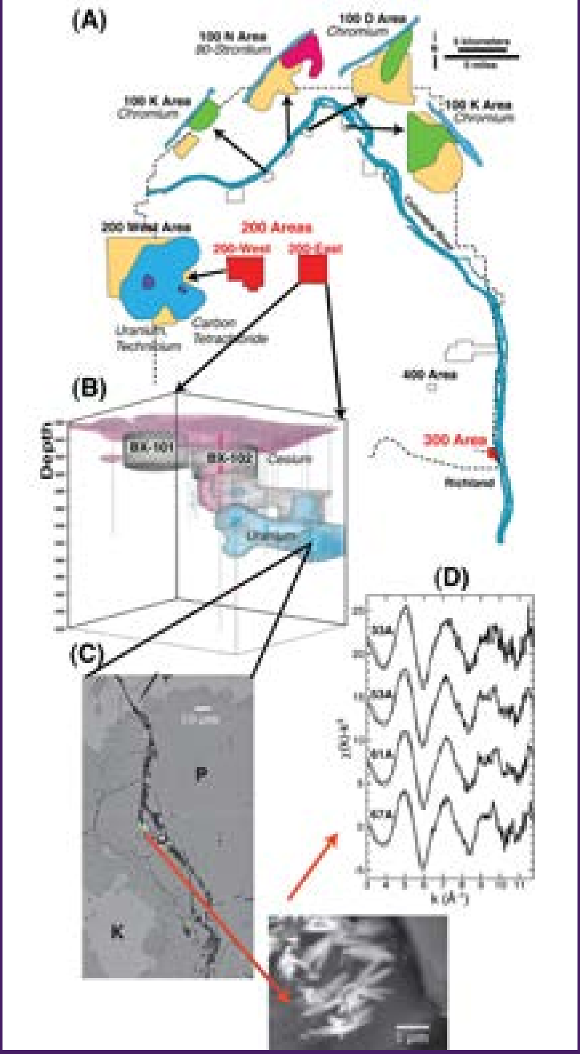
Transient perturbations that occur over short time periods, but result in disproportionately high reaction rates relative to longer intervening time periods, represent an important knowledge gap. Isolated periods of enhanced biogeochemical cycling, termed hot moments, may occur at any spatial (molecular to global) or temporal (millisecond to eon) scale. Although recent research at DOE sites (such as Rifle in Colorado and the Hanford Site in Washington State) has documented how short-term flow path reversals and pressure waves affect plume behavior (Zachara et al. 2013), substantial gaps in understanding these events on spatial scales ranging from square centimeters to square kilometers and on temporal scales ranging from minutes to centuries remain. The need is for information on

- Quantification of the nature, occurrence, and rate of natural hot moments on nutrient and contaminant biogeochemical cycles at different scales
- Prediction of spatial and temporal distribution of hot moments based on underlying hydrologic, geomorphic, microbial, or edaphic patterns
- Development of a new class of remediation approaches based on the combination of natural processes that create hot moments.

There is an important need to understand the relationship of response time to the nature and characteristics of the perturbation event for systems coupled with both abiotic and biotic processes. Integrated field and laboratory investigations, tightly coupled to models, are needed to identify and quantify the underlying mechanisms that produce hot moments of enhanced biogeochemical cycling and control their longevity.

HANFORD SITE WASTE STORAGE, THE VADOSE ZONE, RIVER STAGES

Waste leaks or spills (a) create complex three-dimensional plumes (b), such as the one shown beneath Tank 241-BX-102, where 300,000 liters of waste containing 7 to 8 tons of uranium spilled due to an overfilling incident (Maher et al. 2013), possibly related to a plugged overflow line, in February 1951 (Field et al. 2011). The uranium from the waste reacted in the subsurface beneath the tank and formed solid phase precipitates, predominantly sodium boltwoodite (c,d), which became lodged in subsurface microfractures (McKinley et al. 2006). The uranyl complexes are weakly absorbed to the surface, as shown by the X-ray absorption fine structure spectra (Catalano et al. 2004), and these complexes are responsible for the longer lasting uranium plume (Maher et al. 2013).



Reprinted with permission from (Maher et al. 2013). Copyright 2013, American Chemical Society. Figure D reprinted with permission from Catalano et al. (2004). Copyright 2004, American Chemical Society.

Developing a predictive understanding of how transient perturbations influence subsurface flow and transport across multiple spatial and temporal scales will lead to significant benefits; developing knowledge and models will drive improvements in existing remediation approaches. Entirely new strategies that exploit hot-moment activity to assist in remediation may be developed. Moreover, predictive understanding of emergent processes impacted by transient events will have scientific impacts beyond remediation activities. Examples include predicting the impacts of hydraulic fracturing on deep subsurface biogeochemical cycling for increased energy recovery and understanding of how weather and climate influence subsurface microbiological activity. New scientific insights on surface water eutrophication, toxic algal blooms, hypoxia, heavy metal transport, soil quality, and greenhouse gas fluxes to the atmosphere will result. Given that microbial genomics tools can now inform the variation in metabolic potential and in-gene expression in response to perturbations, better prediction of microbial forcings and responses can have ramifications for managing engineered restoration systems, and even human bodies, leading to novel microbial therapeutics and diagnostics. The future ability to predict when and where high process rates will occur or possible responses to these perturbations in a landscape will ensure the effective management of soil, water, air, and human health resources.

Low-Permeability Domains in Subsurface Materials

The subsurface fate and transport of contaminants is strongly influenced by the presence of low-permeability domains, where diffusive transport dominates over advective transport. These domains may exist within (1) deposits of coarse-textured sands and gravels in the form of fine-grained stringers or lenses of silt- or clay-sized materials or (2) rock fragments and/or soil aggregates as internal interconnected pore or fracture space with complex topology. Low- permeability domains are key subsurface heterogeneities that can dominate the reactive surface area of a given geologic formation and create zones of multiple porosity with different transport, chemical, and microbiologic properties. These low-permeability domains can strongly influence long-term system behavior. Developing new insights and rigorous computational models that bridge the gap between diffusion-dominated interfacial processes and the hydrodynamic flow regime is a scientific grand challenge that will benefit complex site remediation as well as geothermal and oil/gas resources, heterogeneous catalysis, chemical processing, and materials synthesis.

Low-permeability domains function as diffusion-limited sinks for oxygen and other terminal electron acceptors through microbial respiration that occurs within them. Contaminants that diffuse from the advection domain react with microorganisms and high-surface-area mineral material that are concentrated within these zones to alter speciation and mobility. Reacted solutes may be released back to groundwater when conditions change, allowing the low-permeability domain to function as a persistent contaminant source long after primary advective domains have been cleansed by transport or remediation. Source-sink behavior creates chemical gradients at the interfaces of low-permeability domains with primary advective flow paths that may change in complex ways with plume passage and/or remediation. Fundamental challenges exist in determining low-permeability domain volumes and their in situ transport and reaction properties in heterogeneous subsurface materials. In addition, challenges exist in developing robust reactive transport models that properly account for the coupling, mass transfers, and developed gradients between advection- and diffusion-dominated domains that define overall system response.

Low-permeability domains exist in virtually all subsurface systems over the scale range of millimeters to many tens of meters and more. While their behaviors are primarily controlled by the coupling of small-scale chemical and microbiologic processes with diffusive transport, their effects can be manifest over a large range of spatial scales. Their occurrence in hard-to-access subsurface environments has made their study historically challenging, but improvements in instrumentation and measurement modalities at different scales are now making them accessible to research. New opportunities exist that could significantly improve fundamental investigations such as mechanistic, laboratory-based reactive transport studies in model systems or with excised sediments containing hierarchical pore structures at the meter scale and below. Field-based evaluations of low-permeability domains and their impacts within pristine and contaminated subsurface water systems under dynamic hydrologic conditions could also improve these investigations. Advances in specific approaches for chemical speciation enabled by the array of resources at DOE user facilities allow previously unattainable characterization of reaction locations and networks mediated by microorganisms and/or chemical conditions that are different from the bulk fluid. New neutron, electron, and X-ray scattering, microscopy, and tomography techniques now allow multiscale characterization of interconnected pore spaces and pore network topology of intact subsurface materials. This information is critically needed to accurately calculate residence times and transport pathways controlling biogeochemical transformations and contaminant sequestration within low-permeability domains. Recently developed four-dimension geophysical methods may allow imaging of in situ biogeochemical processes within and surrounding reactive low-permeability domains in the field (Hubbard et al. 2008; Wainwright et al. 2014 and 2015). However, high-performance, scale-aware computing hardware and software must be adapted to support the interpretation of these measurements within stochastic frameworks and their assimilation into multiscale models to identify low-permeability domain locations, volumes, transport properties, and contributions to system behavior.

These new capabilities will contribute to understanding and predicting transport and biogeochemical processes in heterogeneous, multiporosity subsurface systems that are common to complex remediation sites. Fundamental insights on the subsurface microbiology and geochemistry of pore networks of different size, continuity, and mineral makeups has the potential to identify unique reactive environments influencing contaminant behavior. Process-based knowledge will enable predictions of residence and reaction timescales in low-permeability domains and gradients that form at their interfaces to influence macropore solution compositions. Improved reactive transport models will couple biogeochemical and transport processes occurring in advection- and diffusion-dominated domains. Coupling the processes will allow scientists to better describe the relationships of subsurface geologic structures and low-permeability domains to nonequilibrium transport behavior at the system scale. The benefits to complex remediation projects could be substantial. The resulting multiscale understanding and models of low-permeability domains would provide enhanced capabilities to model the emergent behaviors of groundwater plumes, while a robust understanding of low-permeability domains as long-term sources would provide insights necessary to develop effective remedial methods for persistent contaminants and plumes.

4D Sensing of Reactive Transport

Developing a predictive understanding of flow and transport is hindered by the hidden nature of the subsurface. Subsurface remediation would benefit from characterizing a wide range of hydrological, geochemical, and microbiological properties and their couplings that occur within a heterogeneous framework (Figure 5). The characterization work is hampered because subsurface sampling conventionally relies on borehole-based measurements and sampling. Breakthroughs are needed in realizing in situ characterization of reactive transport properties and processes in four dimensions (three spatial dimensions as well as time), across broad spatial and temporal domains—the mineral (atomic) to the plume (miles) scales that will allow predictions to be made over timescales from fractions of a second to years.

The trend of ubiquitous sensing of the environment, evidenced by recent developments in environmental geophysical techniques (Binley et al. 2015; Hubbard and Linde 2011), fiber-optic technologies, and unmanned aerial vehicles offers great promise for vastly improved characterization of contaminated sites. Further development of these and completely new sensing approaches that can remotely and autonomously sense subsurface hydrological, geochemical, and biological properties are needed, including approaches that provide useful but indirect information or that respond to an induced perturbation. Examples include development of approaches for quantifying interfacial biogeochemical transformations from the pore to plume scale (Revil et al. 2012; Williams et al. 2005) and development of proteome microdevices that could be inserted in the subsurface to quantify and transmit information on enzyme activity associated with critical biogeochemical transformations.

Extracting information from proxy measurements and integration with direct measurements and models offers promise of transitioning beyond the characterization of parts of a contaminated system to a seamless monitoring of integrated and multiscale system behavior. A significant and overarching challenge is to develop new computationally based approaches to co-acquire and couple multimodal (multitype, multiscale) streaming data sets into reactive transport models. Such a capability would revolutionize the understanding of subsurface system behavior over wide space and timescales. Joint or coupled models that consider geophysical, hydrological, and geochemical phenomena and data sets have been developed and used to understand flow and transport at DOE sites (Kowalsky et al. 2005 and 2011). However, these approaches need to be significantly extended to explore how hot spots and hot moments contribute to integrated system hydro-biogeochemical system behavior. To meet this challenge, petrophysical relationships that link sensed observables with target properties and/or processes across scales must be developed. For example, induced polarization results from the dynamics of the electrical double layer formed at the interface between aqueous solutions and mineral surfaces whose charge is related to the pH and chemical composition of the solution. Thus, if properly calibrated against synthetic and real geomaterial properties, induced polarization signals could be adapted to estimate geochemical properties from nanometer to plume scale. Relationships that incorporate multiple types of sensed observables must also be developed, including relationships obtained from direct and remote or indirect approaches. The following sidebar illustrates the use of surface seismic and borehole approaches to estimate the spatial distribution of reactive facies, including associated geological, hydrological, and mineralogical estimates. In addition to mechanistic, coupled modeling approaches, research into data-driven approaches is needed to take advantage of multimodel, time-lapse data sets in complex systems, particularly where mechanistic linkages between observables are limited. An example of this type of approach is shown in the following sidebar, which illustrates the use of time-lapse, spectral-induced polarization data to estimate iron(II) oxide concentration evolution following biostimulation of the uranium-contaminated subsurface at the Rifle site in Colorado (Chen et al. 2012).

The scientific impact realized by developing four-dimensional reactive sensing approaches will transform the ability to understand and ultimately predict the myriad processes that occur in the subsurface across broad temporal and spatial scales. Seamless integration of different data types, including laboratory- and field-based direct and indirect measurements, offers the potential for greatly enhanced understanding of heterogeneity and controls on chemical transformations that influence functioning of complex systems: from contaminated environments to subsurface energy reservoirs, ecosystems, human systems, and space exploration. The fundamental understanding of geophysical and microbiological signatures gained through this research, as well as the rapid identification of small-scale controls that drive larger system behavior (and vice-versa), will be broadly relevant. The benefits to environmental management are expected to be significant, leading to an improved ability to predict contaminant fate and transport and optimized remediation and long-term monitoring strategies for subsurface contamination as well as engineered disposal facilities.

GEOPHYSICAL APPROACHES FOR CHARACTERIZING CONTROLS ON URANIUM PLUME MOBILITY AND FOR MONITORING REMEDIATION

Reactive facies represent a package of sediments having a unique distribution of physico-chemical properties relative to surrounding regions that influence plume mobility (Sassen et al. 2012). At the uranium-contaminated Savannah River Site F-Area, seismic and wellbore data were used to estimate the spatial distribution of reactive facies along a uranium plume centerline (Figure A) (Wainwright et al. 2014). Use of reactive facies to parameterize reactive transport models at the F-Area demonstrates the improved prediction of decadal-scale uranium plume migration compared to use of only physical or geochemical properties to constrain the model (Figure B) (Bea et al. 2013). Use of time-lapse spectral-induced polarization to monitor microbially induced subsurface transformations leading to iron(II) production was also tested in conjunction with a bioremediation treatment at the uranium-contaminated Rifle, Colorado, floodplain site (Chen et al. 2012). The geophysical monitoring significantly improved understanding of the evolution of bioremediation-induced groundwater chemistry relative to what could be inferred based on wellbore data alone (Figure C).

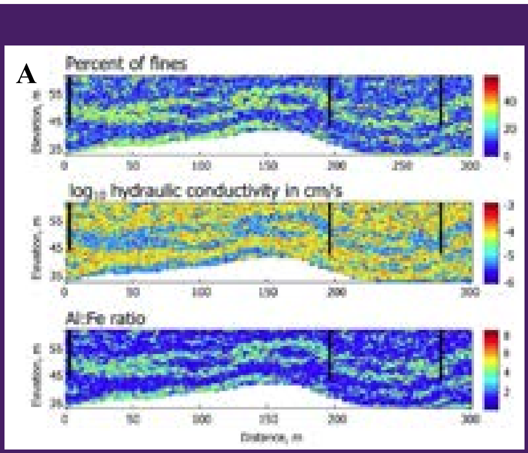
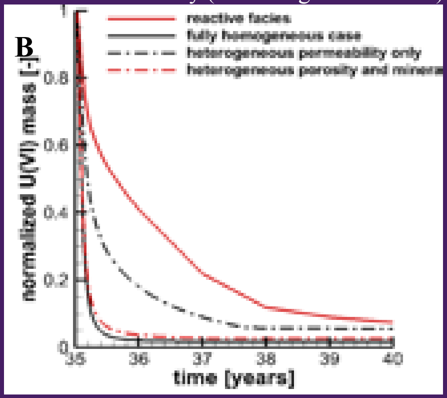


Image courtesy of Susan Hubbard Lawrence Berkeley National Laboratory (Wainwright et al. 2014)



Reprinted by permission from
John Wiley and Sons: Wiley Online Library,
Haruko Wainwright, et al., Copyright 2014

(a) Geophysically obtained estimates of reactive facies along a 300 m uranium plume centerline, illustrating within facies variability of sediment texture, hydraulic conductivity, and sediment geochemistry that influences sorption; (b) simulated mass of same uranium plume past a downgradient control plane, performed using model parameterizations that included reactive facies physico-chemical estimates, chemical heterogeneity only, and physical heterogeneity only;
(c) comparison of subsurface system response to uranium bioremediation at the Rifle, Colorado, site using interpolated wellbore information (left) and time-lapse geophysical data (right). Figures show the concentration of iron(II), which is indicative of the redox status altered by the remediation approach.

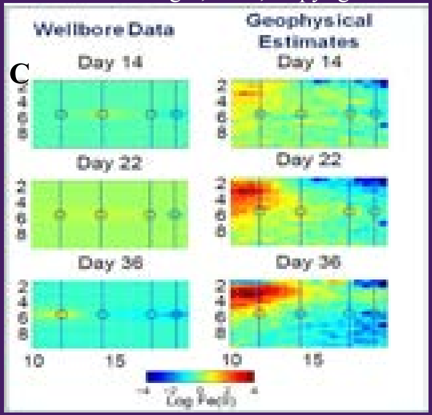


Image courtesy of Susan Hubbard, Lawrence Berkeley National Laboratory (Chen et al. 2013)

Predicting Emergent Behavior of Multiscale Systems

The complexity of the subsurface, as shown in Figure 5, absolutely necessitates the use of models to incorporate understanding of multiscale properties, processes, and their interactions for prediction of contaminant fate and transport, and optimized design of remediation strategies. Computational advances are needed to accurately simulate bidirectional coupling between processes across highly disparate spatial and temporal scales. With impending exascale computing capabilities and an advancing deluge of observational data (ranging in scales from atoms to the globe and based on measurements ranging from laboratories to satellites), a significant opportunity now exists to develop advanced multiscale modeling and data interpretation and assimilation capabilities, leading to vastly improved subsurface fate and transport predictions.

Characteristics of current subsurface fate and transport prediction capabilities underscore the need for new computational advances. Currently, fundamental (first principles) models cannot directly inform application-scale models, which tend to be highly parameterized and empirical in nature. Single-scale process models are well developed across a range of scales; direct connections among models at diverse scales are currently limited by computational demands. Diverse data sets are now becoming available, but few capabilities exist to rapidly assimilate heterogeneous information into models for improved real-time predictions. Due to structural and parameter uncertainties, models can currently not be used to decipher how (and under what conditions) coupled microscale processes are manifested in system-scale behavior.

The development of scale-aware computational methods for adaptive, bidirectional coupling across molecular-, pore-, continuum-, and plume-scale models are needed. Across these scales, capabilities to probe and simulate molecular- through pore-scale processes, and their emergent impacts on field-relevant contaminant fate and transport, are particularly needed. The need for advanced, scale-aware, data-driven discovery methodologies, paired with model development, exists for subsurface data sets.

The scientific impact expected from new computational advances is expected to be significant and broad (DOE 2014). Development of novel, data-driven discovery methods for subsurface data sets and the integration of multimodel data and model outputs across spatial and temporal scales could lead to rapid identification of critical indicators of emergent system responses to small-scale impacts of environmental change. This represents a grand challenge in subsurface science that could have enormous impact. For example, new modeling methods could be used to identify and ameliorate sources of model error in subsurface simulations, improving predictive understanding of complex subsurface systems. Developed capabilities are expected to be useful for water resource work, predictive agriculture, subsurface energy production, and carbon cycling.

The potential impacts of exascale modeling capabilities are clear. Advanced predictions will lead to vastly improved site conceptual models that properly represent emergent effects of fundamental microscale mechanisms. Models that accurately predict flow and transport, now and in the future, are expected to lead to a new class of contaminant control and attenuation strategies that are sustainable and cost effective over decade-to-century timeframes. An improved understanding of key controls on flow and transport (at different locations, scales, and timeframes) can be used to design optimized, long-term monitoring strategies.

Conclusions

An extremely important and complicated veneer of the planet, the shallow subsurface hosts water resources, supports agriculture, and plays a critical role in biogeochemical cycling that supports most life on Earth. Unfortunately, it also holds a significant volume of EM legacy waste, notably including metals and radionuclides that do not degrade naturally over time to benign products. Understanding plume mobility and scientific underpinnings to guide successful remediation over timescales relevant to the EM mission is hampered by the multiscale complexity of this shallow system.

Several specific research opportunities were identified by the subsurface flow and transport panel, which complement previously identified Grand Challenges. Given the complexity of the subsurface, the importance of jointly and iteratively advancing the identified process understanding, observational, and prediction-based research challenges is emphasized.

Realization of the proposed advances will result in research that could rapidly transform responsible and sustainable management of contaminated (and other shallow subsurface) systems. In addition, the proposed advances could transform deeper subsurface environments that support over 80 percent of the US energy and store geologically sequestered carbon dioxide and nuclear waste.

References

Bea S, H Wainwright, N Spycher, B Faybishenko, SS Hubbard, and M Denham. 2013. "Identifying Key Controls on the Behaviour of an Acidic-U(VI) Plume in the Savannah River Site using Reactive Transport Modeling." *Journal of Contaminant Hydrology* 151(2013): 34-54. DOI: 10.1016/j.conhyd.2013.04.005.

BERAC – Biological and Environmental Research Advisory Committee. 2010. *Grand Challenges for Biological and Environmental Research: A Long-Term Vision*. DOE/SC-0135, US Department of Energy, Washington, DC. http://science.energy.gov/~/media/ber/pdf/Ber_ltv_report.pdf.

BESAC – Basic Energy Sciences Advisory Committee. 2007. *Basic Research Needs for Geosciences: Facilitating 21st Century Energy Systems*. US Department of Energy, Washington, DC. http://science.energy.gov/~/media/bes/pdf/reports/files/geo_rpt.pdf.

BESAC – Basic Energy Sciences Advisory Committee. 2015. *Challenges at the Frontier of Matter and Energy: Transformative Opportunities for Discovery Science*. US Department of Energy, Washington, DC.

Binley A, SS Hubbard, J Huisman, A Revil, D Robinson, and K Singha, and L Slater. 2015. "The Emergence of Hydrogeophysics for Improved Understanding of Subsurface Processes over Multiple Scales." *Water Resources Research* 51(6): 3837–3866. DOI: 10.1002/20015WR017016.

Catalano JG, SM Heald, JM Zachara, and GE Brown, Jr. 2004. "Spectroscopic and Diffraction Study of Uranium Speciation in Contaminated Vadose Zone Sediments from the Hanford Site, Washington State." *Environmental Science and Technology* 38(10): 2822–2828.

Chen J, S Hubbard, and K Williams. 2013. "Data-driven Approach to Identify Field-Scale Biogeochemical Transitions Using Geochemical and Geophysical Data and Hidden Markov Models: Development and Application at a Uranium-Contaminated Aquifer." *Water Resources Research* 49(10). DOI: 10.1002/wrcr.20524.

Chen J, SS Hubbard, KH Williams, A Flores Orozco, and A Kemna. 2012. "Estimating the Spatio-Termporal Distribution of Geochemical Parameters Associated with Biostimulation using Spectral Induced Polarization Data and Hierarchical Bayesian Models." *Water Resources Research* 48(5): W05555. DOI: 10.1029/2011WR010992.

DOE – US Department of Energy. 2010. *Complex Systems Science for Subsurface Fate and Transport*. DOE/SC-0123. US Department of Energy, Washington, DC. http://science.energy.gov/~/media/ber/pdf/SubsurfaceComplexity_03_05_10.pdf.

DOE – US Department of Energy. 2014. *Software Productivity for Extreme-Scale Science (SWP4XS)*. US Department of Energy, Washington, DC. http://www.orau.gov/swproductivity2014/SoftwareProductivityWorkshopReport2014.pdf.

Field JG, LA Fort, and M Wood. 2011. *Hanford BX-Farm Leak Assessments Report.* RPP-RPT, 47562, Rev. 0, Washington River Protection Solutions, Richland, Washington. http://www.hanford.gov/files.cfm/RPP-RPT-47562_-_Rev_00.pdf.

Hubbard SS, K Williams, M Conrad, B Faybishenko, J Peterson, J Chen, P Long and T Hazen. 2008. "Geophysical Monitoring of Hydrological and Biogeochemical Transformations Associated with Cr(VI) Biostimulation." *Environmental Science and Technology* 42(10): 3757–3765. DOI: 10.1021/es071702s.

Hubbard SS, and N Linde. 2011. "Hydrogeophysics." In: Peter Wilderer (ed.) *Treatise on Water Science*, vol. 2, pp. 401–434, Academic Press, Oxford.

Kowalsky MB, S Finsterle, J Peterson, SS Hubbard, Y Rubin, E Majer, A Ward, and G Gee. 2005. "Estimation of Field-Scale Soil Hydraulic and Dielectric Parameters Through Joint Inversion of GPR and Hydrological Data." *Water Resources Research* 41(11): W11425. DOI: 10.1029/2005WRR004237.

Kowalsky MB, E Gasperikova, S Finsterle, D Watson, G Baker, and SS Hubbard. 2011. "Coupled Modeling of Hydrogeochemical and Electrical Resistivity Data for Exploring the Impact of Recharge on Subsurface Contamination." *Water Resources Research* 47(2): W02509. DOI: 10.1029/2009WR008947.

Maher K, JR Bargar, and GE Brown Jr. 2013. "Environmental Speciation of Actinides." *Inorganic Chemistry* 52(7): 3510–3532. DOI: 10.1021/ic301686d.

McKinley JP, JM Zachara, C Liu, SC Heald, BI Prenitzer, and Kempshall. 2006. "Microscale Controls on the Fate of Contaminant Uranium in the Vadose Zone, Hanford Site, Washington." *Geochimica et Cosmochimica Acta* 70(8): 1873–1887.

Pickett STA and PS White. 1985. *The Ecology of Natural Disturbance and Patch Dynamics*, Academic Press, San Diego, California.

Revil A, E Atekwana, C Zhang, A Jardani, and S Smith. 2012. "A New Model for the Spectral Induced Polarization Signature of Bacterial Growth in Porous Media." *Water Resources Research* 48(9): W09545. DOI: 10.1029/2012WR011965.

Sassen D, SS Hubbard, S Bea, N Spycher, J Chen, and M Denham. 2012. "Reactive Facies: An Approach for Parameterizing Field-Scale Reactive Transport Models using Geophysical Methods." *Water Resources Research* 48: W10526. DOI: 10.1029/2011WR011047.

Wainwright H, J Chen, DS Sassen, and SS Hubbard. 2014. "Bayesian Hierarchical Approach and Geophysical Datasets for Estimation of Reactive Facies over Plume Scales." *Water Resources Research* 50(6): 4564–4584. DOI: 10.1002/2013WR013842.

Wainwright H, AF Orozco, M Bucker, B Dafflon, J Chen, SS Hubbard, and KH Williams. 2015. “Hierarchical Bayesian Method for Mapping Biogeochemical Hot Spots Using Induced Polarization Imaging.” *Water Resources Research*. Accepted December 30, 2015. DOI: 10.1002/2015WR017763.

Williams KH, D Ntarlagiannis, LD Slater, A Dohnalkova, SS Hubbard, and JF Banfield. 2005. “Geophysical Imaging of Stimulated Microbial Biomineralization.” *Environmental Science Technology* 39(19): 7592–7600. DOI: 10.1021/es0504035.

Williams KH, JN Christensen, and C Hobson. 2015. “Surface Water-Groundwater Interactions as a Critical Component of Uranium Plume Persistence.” Presented at the *American Geophysical Union 2015 Fall Meeting, San Francisco, California, December 14-18, 2015*. Abstract H31l-1546.

Zachara J, PE Long, JA Davis, P Fox, MD Freshley, AE Konopka, C Liu, JP McKinley M Rockhold, KH Williams, and SB Yabusaki. 2013. “Persistence of Uranium Groundwater Plumes: Contrasting Mechanisms at Two DOE Sites in the Groundwater-River Interaction Zone.” *Journal of Contaminant Hydrology* 2013: 45–72.

ELUCIDATING AND EXPLOITING COMPLEX SPECIATION AND REACTIVITY FAR FROM EQUILIBRIUM

Abstract

EM's wastes involve extreme chemical and physical conditions that are far from equilibrium, making prediction of their behavior as the materials are processed or stored as long-term waste forms nearly impossible at present. When adequately described, even simple aqueous solutions containing dissolved species involve significant complexity. In the case of EM tank wastes, the complexity is exacerbated by high pH and ionic strength, and the presence of high radiation environments or radioactive materials. In the case of structural materials and materials used in waste forms, the lack of knowledge of the impact from extreme environments prevents development of new materials with long-term stability and optimized performance. Accurately representing all aspects of such systems and confidently predicting their changes in time and space is a monumental task. If effectively elucidated, this task can lead to identifying unrealized functionality and exploit the chemistries for resiliency in processing streams and materials behaviors. In this PRD, opportunities to address research challenges in the bulk solution and materials systems are discussed; in the PRD titled *Understanding and Controlling Chemical and Physical Processes at Interfaces* an additional dimension of complexity confronting these systems and interfacial processes is addressed.

Scientific Challenges

The materials and solutions in the high-level radioactive waste tanks represent extremes in chemical conditions that are quite far from equilibrium and result in unexpected speciation and reactivity. Factors that drive these conditions are unique and include high levels of ionizing radiation, concentrated electrolytes, and extremes in alkalinity. Despite the lack of predictability in the chemistry of these waste streams, they must be safely processed and stabilized for disposal. The processing is intended to partition the highly radioactive components from the less radioactive bulk materials, resulting in high- and low-level radioactive waste forms. Safety requirements coupled with limited confidence in predicting chemical behavior severely restrict EM's ability to effectively and efficiently process the tank wastes and produce acceptable waste forms.

Chemically harsh systems that include a radiation environment embody a complicated, multifaceted grand challenge for scientific understanding and prediction. The current understanding of the speciation and reactivity of fission product and actinide elements is based on much simpler systems that are generally at equilibrium. Consequently, it is not possible to predict oxidation states, chemical forms, or reaction pathways in these unique systems. For EM tank wastes, the radiation environment has existed for decades. Long-term radiolysis has caused continuous production of metastable, reactive species that can drive unexpected chemical transformations and create unanticipated species. When considering materials used in waste processing and waste forms, the coupled effects of radiation damage in materials along with poorly understood chemistry are challenges. Developing safe waste processing schemes and effective waste forms requires mastering and exploiting the chemical behavior of these systems that are far from equilibrium. In the case of waste processing and waste forms, a greater understanding of the myriad chemical and physical processes occurring in these solutions and materials is needed to accelerate the development of new processes and materials required for EM's mission.

Understanding Radiolysis and Radiation Effects to Predict Unique Species in Radioactive Waste Systems

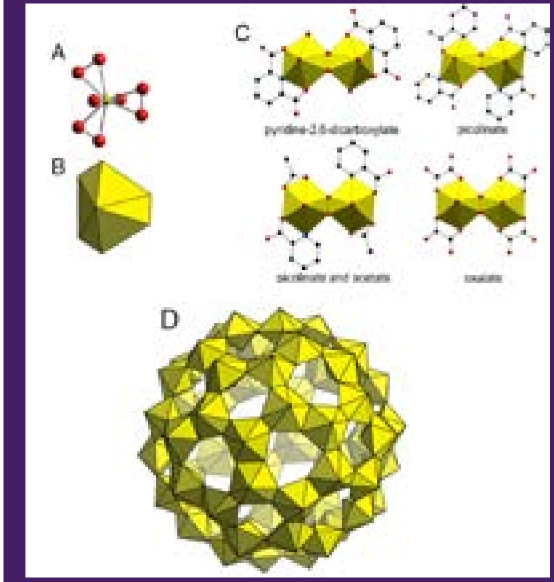
As described in the *Waste Stream Characterization, Transformation, and Separations* section, radiation generates transient but highly reactive species, which likely drive other chemical reactions. Examples are numerous, and one is the generation of peroxides and subsequent complexation by the dioxoactinide species, which leads to the formation of surprising uranium and plutonium species (see sidebar).

SURPRISING EFFECTS FROM SEEMINGLY TRANSIENT SPECIES

Water radiolysis produces peroxide (O_2^{2-}), which is typically considered quite reactive and short lived. In the presence of some dioxoactinide species such as the uranyl cation (UO_2^{2-}) however, peroxide persists when coordinated directly with the metal cation as shown in Figure A and B. In nature, alpha decay of uranium produces peroxide that can lead to the formation of the mineral studtite (for example, $[(UO_2)O_2(H_2O)_4]$), allowing the peroxide moiety to persist for millions of years. In highly radioactive waste tanks, the radiation environment continuously generates peroxide.

The coordination of three peroxide species to one uranyl cation yields the structural building block (Figure B), which can aggregate to form larger structures such as the U_{60} cage structure (Figure D). In other cases, two uranyl cations can coordinate via a single peroxide cation, leaving the remaining uranyl equatorial coordination sites available for complexation with other ligands (Figure C).

Over the past 15 years, many such fullerene-cage architectures based on peroxide coordination of actinyl species have been identified with varying internal cage sizes. This creates an opportunity to exploit the internal cage environments to drive reactivity and functionality (Armstrong et al. 2012).



Uranium structures. Image courtesy of Armstrong et al. (2012).

Much of our existing knowledge on water radiolysis is derived from systems in which water is the matrix. However, in the case of high-level radioactive waste streams and similar EM systems, the extremely high concentration of electrolytes results in water not being a major component of the systems. Consequently, radiolysis likely creates other, currently unidentified, highly reactive, transient species that drive the formation of unexpected chemical species.

Ionizing radiation also causes damage in solid materials, whether they are waste forms (for example, glasses, cements), matrices used for chemical separations, or structural materials such as the alloys used in tanks and processing equipment. As discussed in the *Waste Forms* section the interaction of radiation with solid materials results in the transfer of energy to electrons and atomic nuclei, which in turn produces both electronic and atomic defects that interact to determine the ultimate evolution and potential degradation of the material (Weber et al. 2015). Also, the structure and physical properties of the materials can be significantly altered due to the numerous processes, such as injection of helium and other decay or fission fragments into the structure, and by the intentional creation of defects via ion implantation. At the same time, the basic chemistry of the system evolves because of the decay of radioisotopes from one element to others. In addition to creating defects and changing chemistry, these same processes are accompanied by global and transient heat generation (Weber 2014). Exacerbating the problem is the fact that the damage event caused by ionizing radiation occurs very quickly and produces individual defects that are highly localized, such as atomic collision cascades, electronic excitations, and thermal spikes on the picosecond timescale and the nanometer length scale. However, the damage and resulting defects accumulate over time, leading to a coupling and magnification of their impact over much longer time domains, from years in the case of separations and structural materials to millennia in the case of waste forms. Such atomic-scale alterations can cause a cascade of events that can ultimately lead to materials failure.

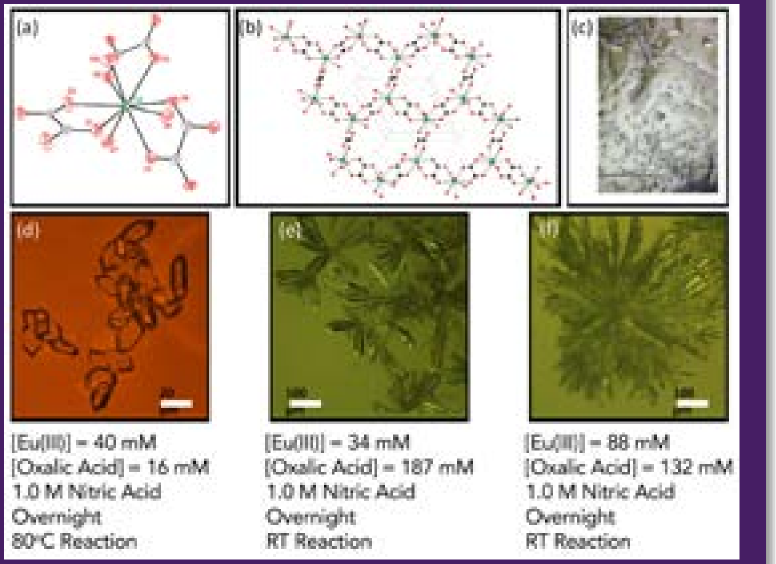
The chemical and physical complexity of both tank wastes and associated structural materials, as well as waste forms, represent huge challenges that must be understood before new processes and materials can be designed. Further, basic thermodynamic, kinetic, and other chemicophysical data that enable prediction of radionuclide speciation and materials behavior are lacking (see sidebar). As described in this PRD and in the *Transformative Research Capabilities* section, opportunities now exist to couple direct observation of chemical species with advanced molecular-level modeling. The synergy between the experimental observation and computational approaches can lead to a fundamental understanding of the chemistry and physics of these systems. This understanding will enable more robust modeling tools and much higher confidence in predictions involving high-level radioactive waste streams and materials that are needed to develop vastly improved and reliable processing and long-term storage technologies.

SOLUTION SPECIATION AND SOLID PHASE NUCLEATION ARE NOT WELL UNDERSTOOD

Designing processing schemes for radioactive wastes requires understanding and mastering the multitude of chemical reactions to enable process control, including precipitation of elements when desired and dissolution of solids when necessary. Past work on actinide complexation by simple organic ligands provides initial foundation equilibrium conditions that describe the coordination chemistry of solution species. How these species organize in solution to homogeneously nucleate into crystalline solid phases is largely unknown.

Oxalate precipitation is often used during the processing of nuclear materials to separate actinide elements from other fission products. An example of a plutonium oxalate complex is trivalent plutonium coordinated by three oxalate anions (Figure A). The structure of the plutonium(III) oxalate solid is shown in Figure B, along with the bluish-purple crystalline needles shown in Figure C.

Europium(III) is a fission product that is often separated during waste processing, along with other lanthanide and actinide elements. In addition, it is sometimes used in developmental studies as a nonradioactive analog for trivalent plutonium. As shown in Figure D-F, its crystalline morphology is affected by the conditions under which it precipitates. While such phenomena are well recognized, it is quite difficult to predict a priori*,* making it challenging to confidently exploit this knowledge to tune solid-phase morphology during processing. A scientific basis for describing the organization of species in EM waste streams, leading to homogeneous nucleation and solid-phase growth, will enable safe next-generation cleanup technologies with improved efficiency and lower costs.



[Eu(III)] = 40 mM
[Oxalic Acid] = 16 mM
1.0 M Nitric Acid
Overnight
80°C Reaction

[Eu(III)] = 34 mM
[Oxalic Acid] = 187 mM
1.0 M Nitric Acid
Overnight
RT Reaction

[Eu(III)] = 88 mM
[Oxalic Acid] = 132 mM
1.0 M Nitric Acid
Overnight
RT Reaction

Plutonium oxalate precipitation (top) and europium(III) precipitation (bottom). The plutonium oxalate complex (a) is trivalent plutonium coordinated by three oxalate anions. The structure of the plutonium(III) oxalate solid (b) is shown, along with the bluish-purple crystalline needles (c). Europium(III) is affected by the conditions under which it is precipitated. Top image: Adapted with permission from Runde, et al. (2009). Bottom image courtesy of Pacific Northwest National Laboratory.

Chemical Reactivity and Reaction Networks for Complex Systems in Radiation Environments

The environments of waste streams and waste forms relevant to the EM mission are highly complex and dynamic, and their behavior defies representation by simpler model systems. The complexity of the wastes, driven by extremes of pH, ionic strength, and especially ionizing radiation, continuously generates transient species that force unexpected chemical reactions. As a result, chemical and physical mechanisms that might be understood individually compete with each other, leading to counterintuitive behavior in the aggregate. For example, the rheology of many of the high-level radioactive waste streams prevents rapid, homogeneous mixing. Consequently, chemical environments may cycle episodically. During tank waste processing, chemical compositions of solids that are entrained in the waste streams may vary significantly, and these solids are not in equilibrium with the solution phase. The radiation field (which is derived from the radioactivity of the entrained solids) likely varies, and the generation and/or accumulation of radiation-induced transients and gases can be unpredictable. The rates of these reactions and their influence on the overall outcome currently cannot be predicted with the level of confidence that is vital to develop new processing and storage technologies, which are central to the success of EM's mission.

Consequently, a huge gap exists in understanding the relative contributions of the multitude of chemical species and their reaction networks to the evolution of the overall system, whether waste solutions or materials. Predictions over large temporal and spatial scales cannot be extrapolated from simple experiments without an adequate mechanistic understanding of the overall system. This knowledge gap also prevents exploitation of transient species and unexpected reaction mechanisms to enable control of reactivity and design of resilient materials for applications in radiation environments.

To illustrate the point with an example of solid phase materials behavior, it is not possible to credibly conduct experiments at elevated temperatures to accelerate defect-healing rates and assume that the same pathways prevail at ambient conditions where overall rates are too slow to measure. Understanding these mechanisms requires an intimate coupling of experiment and modeling across many dimensions of information to fully elucidate how parameters such as temperature, the nature of the irradiation source, and material structure collectively yield the relevant material evolution as a function of conditions.

In summary, this PRD focuses on elucidating the myriad chemical reactions that occur in the bulk of complex waste streams and waste forms, which are the species that react at interfaces in the PRD titled *Understanding and Controlling Chemical and Physical Processes at Interfaces.* For the non-interfacial, bulk processes described, research efforts should be focused on

- Understanding complex chemical equilibria to enable prediction and control of speciation
- Understanding and exploiting chemical reactivity in complex systems.

Recent advances in dynamic chemical imaging and computational capabilities (see also the *Transformative Research Capabilities* section) hold the potential for examining these complex systems in real time and under relevant conditions that will provide—for the first time—the insight required to develop efficient, cost-effective, and safe technologies to handle EM wastes for years to come.

Research Directions

The matrices and materials that make up high-level radioactive wastes are heterogeneous chemical systems that are quite far from equilibrium. In processing the radioactive wastes to generate waste forms for disposal, operational control is essential for the safe and cost-effective treatment of the materials.

Understanding and predicting the chemical form and reactivity of the constituents in the waste streams are essential for developing processing schemes, and coupling speciation with reactivity in extreme environments may enable revolutionary new approaches to highly radioactive waste treatment.

Understanding Complex Chemical Equilibria to Enable Prediction and Control of Speciation

The chemical and physical complexity of systems associated with EM wastes has precluded the level of knowledge needed to meet EM's mission. Basic thermodynamic, kinetic, and other chemicophysical data that enable prediction of radionuclide speciation in these waste streams are lacking. For example, the recent observation of monovalent technetium species in high-level radioactive waste systems was quite unexpected. Clearly, the knowledge of speciation and reactivity in systems involving redox equilibria, concentrated electrolytes, and ionizing radiation is extremely limited or in some cases nonexistent. The generation of the basic mechanistic foundation to describe redox reactivity in these systems is clearly needed, and we can build from knowledge derived from other EM problems. For example, significant effort has been invested to describe actinide speciation in concentrated electrolytes in support of the disposal of transuranic waste in the Waste Isolation Pilot Plant (Neck et al. 2009). While this past effort has resulted in thermodynamic data to describe radionuclide speciation in brines, this understanding does not readily translate into many other EM-relevant systems.

Current state-of-the-art processes for understanding contaminant equilibria in concentrated brines treat changes in ion pairing and charge shielding empirically, which results in the development of apparent activity coefficients. Consequently, these activity coefficients are only relevant for the specific system under which they were developed. Systems such as these radioactive waste streams are much more complex than salt-based disposal geomedia. While the concentration of electrolytes is quite high in both systems, the complexity of the electrolyte compositions is far greater in the high-level radioactive waste streams at EM sites. In addition, the quantity of ionizing radiation in the radioactive waste systems is many orders of magnitude greater than that in the salt disposal medium. Furthermore, the high-level radioactive wastes in EM have been exposed to ionizing radiation for many decades, whereas the salt disposal medium has not yet experienced exposure to significant levels of ionizing radiation.

In typical laboratory-based experiments, radiolysis is known to alter chemical speciation because of the reactive species it produces in the solvent, which is typically water. In the case of both natural brines and high-level radioactive wastes, water is actually a minor component and behaves more as a solute than a solvent. As such, the current knowledge of chemical species resulting from radiolysis in water is not directly applicable to EM's high-level radioactive waste systems. Therefore, an important research need is to define relevant radiolytic reactions occurring in concentrated electrolytes. Although a specific species might be considered transient, when all of the species in these systems are taken in total, their production may be continuous over decades, which can drive unexpected reactions. As radiolytic species are identified, their impact on other processes, such as reduction-oxidation reactions and other complexation reactions, must be determined.

The ability to advance understanding of complex speciation in the presence of ionizing radiation will require the close coupling of experimental and theoretical methods, as detailed in the *Transformative Research Capabilities* section. The ability to determine bulk, trace, and transient constituents experimentally in complex solutions in situ and in real time is critical. Spectroscopic tools are needed to directly determine solution species and how they evolve during radiolysis and also as they relate to events such as hydrolysis, nucleation, and solid phase growth. Molecular dynamics simulations of ions in water alongside organic molecules and radiolysis products to create "realistic" solutions will enable a more detailed understanding of how each constituent impacts the system's chemistry. Such simulations can also be used to evaluate a virial expansion of ion interactions, leading to excess Gibbs energies and activity coefficients. These theoretical techniques require significant advances in the descriptions of the underlying physics of intermolecular interactions in complex fields caused by high ionic strength; advances in these computational tools and exascale computers would enable the full realization of the predictive capabilities of simulations. These advanced simulations will provide insight into solution structure at equilibrium, potentially far from equilibrium, and include how the solution structure and dynamics change during phase transformations.

To make progress in understanding the full range of chemical and physical processes that occur in wastes, it is critical to understand the linkage between dissolved species and precipitates, and the relevant equilibria linking these ends of solubility. Although specific research needs for interfacial processes are addressed in the following PRD, *Understanding and Controlling Chemical and Physical Processes at Interfaces*, the gaps in knowledge for interfacial processes are intimately tied to the equilibria and speciation research needs described in this PRD. The chemical and physical phenomena leading to the organization of species in solution that result in homogeneous nucleation, and ultimately solid phase growth, are poorly understood, even in the simplest of systems.

Today, experimental tools exist to enable an understanding of the coordination chemistry of dissolved species, and advances in microscopy and chemical imaging now allow direct observation of features on sub-nanometer-sized materials. However, experimental observation of homogeneous nucleation in solution remains a technical challenge. In this case, most current insights are derived from computational capabilities. At the same time, recent advances in the spatial resolution of spectroscopic tools, such as high-resolution ultrasound spectroscopy, neutron scattering, advanced light sources, and spatially resolved mass spectrometry, show tremendous promise for observing homogeneous nucleation in real time. As described in the *Transformative Research Capabilities* section, advances in characterization and computational tools provide a compelling opportunity to further understand the complexity and heterogeneity of high-level radioactive waste systems. Such growth in our fundamental knowledge of chemical equilibria in these complex systems will enable confident speciation predictions. These advances will also enable manipulating a system’s chemistry to control the speciation, ultimately leading to improved processes for handling these wastes.

Understanding and Exploiting Chemical Reactivity in Complex Systems

While understanding the relevant chemical equilibria and their thermochemical parameters is important for predicting and controlling speciation in waste streams and waste forms, defining the mechanisms and rates of the various pathways is also very important. Chemical transformations can occur across multiple length and timescales, and the definition of a “reaction pathway” for a process is an incredibly challenging task. New frameworks are needed for defining mechanisms or reaction pathways to provide models of the waste tank or waste form chemical environment.

For example, simulation tools are needed that couple mass balances, thermodynamic information, rates of solute and colloid transport, gas evolution, and rate coefficients for an array of important reactions and chemical compositions. When implemented in massively parallelized architectures, these tools can be deployed at leadership-class computing facilities to predict the array of chemistries resulting from a heterogeneous distribution of reacting materials in the presence of incomplete mixing. These models must be developed and informed by knowledge of the chemistry and hydrodynamics in various waste systems. As an example, such predictive models could quantitatively account for the accumulation of actinide elements and fission products in tanks as waste streams are processed. They could be validated by comparison to individual tanks, most of which differ in overall composition, and could be employed within a feedback loop to create systematically improved approximations across length and timescales.

Such a model could identify key physical or chemical information that is now inadequately described and should be acquired at a high priority (Hobbs 2012).

Materials exposed to extreme environments present another major challenge. Exposure to ionizing radiation typically accrues damage such that these materials can evolve from well-ordered systems into significantly more amorphous systems. This evolution of the material is governed by multiple processes occurring at variable rates. In particular, for processes occurring at low flux rates and at low temperatures, their timescales can be extremely slow, but are the critical processes for dictating the material's final evolution. Compounding this situation is the fact that numerous kinetic processes have similar rates; thus, the rates that dominate are very sensitive to conditions: temperature, fluxes, irradiation sources, and detailed structure of the material. This means that accelerated testing experiments must be done with care, as even small changes in any condition might change the hierarchy of rates and thus the final state of the material. An obvious example is the fact that ceramics that are easy to amorphize at one temperature are impossible to amorphize at higher temperatures because of the relative rates of defect production versus defect recombination (Brown and Williams 2001).

In such cases, it is critical to supplement experimental studies with integrated modeling to identify key mechanisms. Further, these models must account for all relevant kinetic processes so that temporal boundaries between different emergent behaviors can be identified as a function of conditions. These methods must account for, and efficiently treat, the large number of competing reactions. This will enable determination of effective nonlinear aggregate behavior over long times. Kinetic rates must be identified, whether by experiments or modeling, and the latter must be validated, when possible, by experiments.

The properties of materials can be dominated by chemistry, and mastering this chemistry will enable possible exploitation for improved control during materials synthesis and enhanced functionality. For example, solutes may be added to increase strength, provide corrosion resistance, and enhance electronic properties. The chemistry can be controlled during synthesis or changed via ion-beam implantation or even by incorporation of radioisotopes that evolve with time. As these chemically diverse species interact with irradiation-induced defects, they redistribute, precipitating new phases or changing the host structure's stability. Implantation leads to relatively instantaneous changes in local chemistry as a result of copious radiation damage, providing further impetus to structural evolution. In the case of radioisotopes, this chemistry evolves with time, leading to elements that are chemically distinct from the original isotopes and that may be more or less stable in the surrounding matrix than the original nuclides. This further complicates understanding these systems as the equilibrium state of the system is continuously evolving.

Elucidating these processes requires integrated theoretical and experimental efforts, as described in the *Transformative Research Capabilities* section. For example, understanding the processes that occur in irradiated materials will need a multitude of characterization and computational methods. These include experimental spectroscopic, calorimetric, and in situ microscopic studies of radiation damage, ion irradiation, implantation, and/or annealing. Such direct observation must be combined with computational modeling (across scales from atomistic to continuum) using phase-diagram information from Computer Coupling of Phase Diagrams and Thermochemistry supplemented by ab initio data of possible metastable and/or nonequilibrium phases that might occur. Furthermore, accelerated molecular dynamics and kinetic Monte Carlo methods must be used to assess kinetic pathways and their impact on the material's evolution. A key need in this area is high-quality charge-transfer potentials that can accurately account for the behavior of chemical species in a wide range of atomic environments, and in the presence of electronic and atomic defects, to serve as the foundation of atomistic modeling efforts.

Thus, integrated experimental and theoretical approaches are absolutely vital to advancing the understanding of these materials as they complement each other, filling gaps and providing validation that are impossible with one or the other alone. In addition, design studies are needed that extend the overlap between experimental characterization and theoretical tools.

Technology Impacts

The need to quantify chemical equilibria and reactivity beyond the domains of our current understanding is essential for expanding the operational parameters for high-level radioactive waste processing and storage. This knowledge gap results in limited confidence for predicting chemical behavior in harsh systems coupled with ionizing radiation, which forces very conservative and costly operational parameters. The research directions described will also inspire development of advanced computational models that will ultimately enable the prediction of tank composition and reactivity across multiple length and timescales. These computational tools will support rational manipulation of waste processing streams and waste forms that may enhance our ability to provide safer, timelier, and cost-effective designs for the engineered systems. The anticipated advances in theory and simulation will have an impact that extends well beyond the immediate need of EM to understand tank chemistry, weathering of storage materials, or the fates of contaminants.

Development of new statistical mechanical models for high-ionic-strength electrolyte solutions will benefit many fields immediately, such as corrosion science, battery technologies, and geochemistry. In geochemistry, for example, this research would support advances in carbon sequestration in saline aquifers, evaporite evolution, and even atmospheric chemistry via sea-salt aerosols.

Two defining qualities of these environments that concern EM are the complexity of reaction networks and the potential for highly reactive radiation products. Both present theoretical and analytical challenges. Development of reaction-path models, which couple chemical reaction and transport rates in an enormous network, will only advance with a new generation of methods to sample and characterize these difficult chemical environments (described in the *Transformative Research Capabilities* section).

These research directions also will impact many areas of materials science, such as advanced nuclear waste forms, materials for nuclear energy systems (both fission and fusion), and materials for deep space exploration. Through the research directions proposed here and in the subsequent PRD, *Mastering Hierarchical Structures to Tailor Waste Forms*, new design principles will likely emerge. This work will support greater understanding that could lead to the development of radiation-tolerant and resilient sensors for nuclear applications, and understanding and predictive modeling critical to devices employed in high radiation environments. This work will also accelerate the development of industrial fabrication processes derived from accelerator-based electron and ion sources to modify or functionalize materials.

Clearly, progress in the research areas can create an opportunity to exploit unknown and unrealized functionality related to time-dependent behaviors of EM tank wastes and waste form systems. However, these emergent functionalities that will enable next-generation disruptive technologies first require mastery of complex chemical behavior that is far from equilibrium under extreme conditions relevant to high-level radioactive waste streams, the materials used to process the waste streams, and the waste forms that will sequester them for tens of thousands of years or more.

References

Armstrong CR, M Nyman, T Shvareva, GE Sigmon, PC Burns, and A Navrotsky. 2012. “Uranyl Peroxide Enhanced Nuclear Fuel Corrosion in Seawater.” *Proceedings of the National Academy of Sciences of the United States of America* 109(6): 1874-1877.

Brown RA and JS Williams. 2001. “Crystalline-to-Amorphous Phase Transformation in Ion-Irradiated GaAs.” *Physical Review B* 64(15): 155202. DOI: 10.1103/PhysRevB.64.155202.

Hobbs D. 2012. *Form and Aging of Plutonium in Savannah River Site Waste Tank 18*. SRNL-STI-2012-00106, Savannah River Site, Aiken, South Carolina.

Neck V, M Altmaier, TM Rabung, JT Lutzenkirchen, and TJ Fanghanel. 2009. “Thermodynamics of Trivalent Actinides and Neodymium in NaCl, $MgCl_2$, and $CaCl_2$ Solutions: Solubility, Hydrolysis, and Ternary Ca-M(III)-OH Complexes.” *Pure and Applied Chemistry* 81(9): 1555–1568.

Runde W, LF Brodnax, G Goff, AC Bean, and BL Scott. 2009. “Directed Synthesis of Crystalline Plutonium(III) and (IV) Oxalates: Accessing Redox-Controlled Separations in Acidic Solutions.” *Inorganic Chemistry* 48(13): 5967–5972. DOI: 10.1021/ic900344u.

Weber WJ. 2014. “Radiation and Thermal Ageing of Nuclear Waste Glass.” *Procedia Materials Science* 7: 237–246. DOI: 10.1016/j.mspro.2014.10.031.

Weber WJ, DM Duffy, L Thomé, and Y Zhang. 2015. “The Role of Electronic Energy Loss in Ion Beam Modification of Materials.” *Current Opinion in Solid State and Materials Science* 19(1): 1–11. DOI: 10.1016/j.cossms.2014.09.003.

UNDERSTANDING AND CONTROLLING CHEMICAL AND PHYSICAL PROCESSES AT INTERFACES

Abstract

As discussed in the PRD, *Elucidating and Exploiting Complex Speciation and Reactivity Far from Equilibrium*, DOE EM wastes are highly heterogeneous and dynamic; however, to fully understand these systems another level of complexity must be examined, namely interfaces. Molecular processes at interfaces with solids, liquids, and gases often drive mesoscale interactions and contaminant distributions across the interfaces. Furthermore, particle-particle interactions can control macroscopic properties, such as flocculation or precipitation and even transport in the environment. For example, risk-driving radionuclides (such as plutonium, americium, curium, technetium, cesium, strontium, and iodine) have poorly understood chemical and physical behavior at interfacial environments. Adding to the complexity of these processes is the fact that many occur in the presence of concentrated electrolytes, highly ionizing radiation, and/or within confined molecular environments. To predict how these systems will evolve, it is essential to understand chemical reactivity and solvent structures at relevant interfaces under dynamic and/or extreme environments; the behavior of solvents and other chemical species in nanoscale, confined environments; and particle-particle reactivity. Once understood, these processes might be controlled to yield interfaces tailored to enhance separation processes. This scientific foundation will also support new innovations in the processing of high-level radioactive wastes, improved sequestration of contaminants in waste forms, and improved environmental remediation of waste sites.

Scientific Challenges

Interfaces and associated physical and chemical processes have a huge impact on EM’s mission. Adsorption of radioactive species on particles, association with colloids, and interactions with other materials can dramatically impact the effective isolation of these highly hazardous materials from the bulk of tank wastes. Interfaces with minerals and suspended matter in the subsurface can impact transport. Further, interactions between particles can lead to agglomeration, impacting the flow of wastes in separation processes and even clogging pipes and valves. A large number of scientific challenges must be addressed to accelerate EM’s cleanup efforts and enable innovation and new technologies related to remediation of both the high-level radioactive waste tanks and contaminated subsurface environments. Understanding interfacial physical and chemical processes in complex systems will address significant issues associated with tank waste processing and contaminants fate and transport in the subsurface environment. This complexity is illustrated in Figure 6.

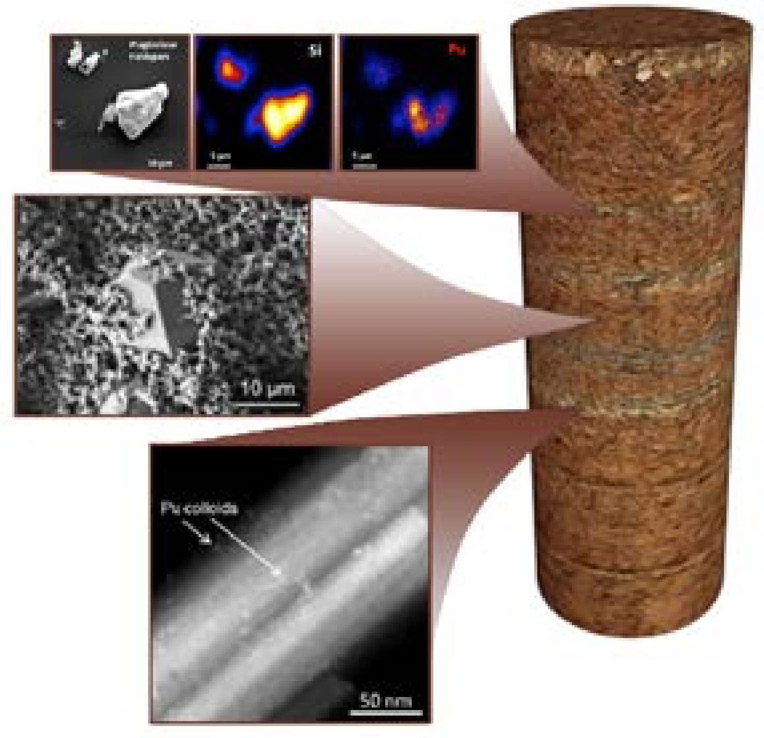


Figure 6. New innovations to enable more timely and cost-effective cleanup alternatives will require an understanding of many complex and heterogeneous interfacial processes in the presence of ionizing radiation. The complexity of the systems relevant to EM, whether stratified wastes in a high-level radioactive waste tank or contaminated soils in the subsurface environment, is shown above. Molecular-level interactions will drive macroscale observables, such as dissolution and precipitation, chemical fractionation, colloidal transport, and slurry rheologies. Image permissions:. Top: Adapted with permission from Kersting (2013). Copyright 2013, American Chemical Society. Middle: Image courtesy of Annie Kersting, Lawrence Livermore National Laboratory. Bottom: Adapted with permission from Powell, et al. (2011). Copyright 2011, American Chemical Society.

High-level radioactive waste streams are highly alkaline slurries of concentrated radioactive materials and electrolytes. As such, the behavior of these waste streams is dominated by interfacial chemical and physical processes that are strongly influenced by ionizing radiation, which often results in counterintuitive observations. For example, finely divided solids that have been exposed to ionizing radiation for decades are often significantly more insoluble than macrocrystalline surrogates that have not been irradiated. Similarly, sonication of waste slurries can increase slurry particle sizes rather than break up the aggregates and dilution of the waste slurry can cause precipitation rather than dispersing and dissolving the solids. Unravelling such mysterious behavior presents a grand challenge due to the multiscale complexity of the heterogeneous waste.

For the high-level radioactive waste tanks, characterization studies to date provide direct evidence on the extreme variability of the materials in the different tanks; as a result, neither the speciation or reactivity of the tank waste components are well characterized. Such variability imposes significant uncertainty on the performance of the waste treatment systems. For example, boehmite, an aluminum mineral phase that makes up a significant fraction of the tank sludge at the Hanford Site exhibits unexpectedly small primary crystal sizes (Figure 7). These small crystals are mixed with microcrystals of many other minerals and the dissolution rate observed for boehmite in this complex environment is much lower than expected. Understanding the cause of this inhibited reactivity is critically needed because it will allow the design of an approach to increase its dissolution rate. An increased dissolution rate could also enable a marked increase in the rate of tank waste processing. Controlling the dissolution and/or precipitation of other contaminants such as chromium, bismuth, iron, and plutonium in the tank wastes during processing are also problematic. Clearly, a knowledge gap exists for understanding and controlling the interfacial reactivity in these complex waste systems.

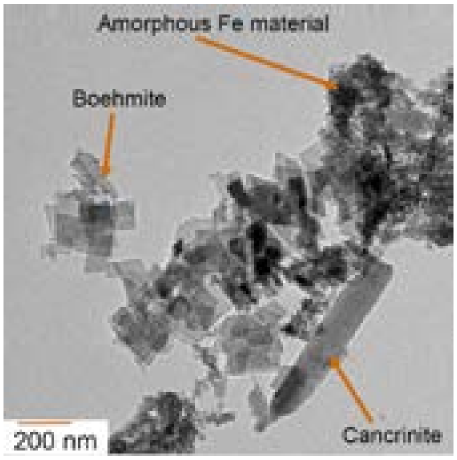


Figure 7. Tank waste is often composed of crystals of varying sizes, which influences reactivity (Russel et al. 2009; Snow et al. 2009). Image courtesy of Pacific Northwest National Laboratory.

Similar challenges exist for subsurface remediation, although the specific conditions and processes differ. For example, the influence of mineral surfaces and colloids on contaminant behavior can lead to unexpected macroscopic results. In some cases, these interfaces can sequester contaminants, and in other cases, they can accelerate contaminant movement in the subsurface. In addition, natural systems can be perturbed by seasonal processes, such as the cycling of nutrients, or they can be disturbed by rare climactic events such as flooding. Effective remediation of subsurface systems requires an ability to predict changes in contaminant behavior from changes in species and concentrations that arise during unexpected events or natural cycles that may occur repeatedly over long timescales. Additional information on subsurface processes is outlined in the PRD, *Predictive Understanding of Subsurface System Behavior and Response to Perturbations*.

Interfaces, including solid-solid, solid-liquid and liquid-liquid, are in essence defects or discontinuities that have different chemical reactivities compared to the bulk material. Interfaces drive much of the reactivity in natural and engineered systems; examples include biological membranes that are essential for sustaining life, mineral-water interfaces that can control contaminant behavior in the environment, and engineered interfaces that enable chemical separations. Such system heterogeneities are directly tied to temperature and thermal properties that typically give rise to disorder and entropy, which can drive interfacial dynamics in unexpected directions. Because of their complexity, interfacial systems have typically been treated in idealized manners, both experimentally and computationally, such that averaged structures or “frozen” states are represented. Such simplifications can miss many of the nuances of structure and dynamics at a molecular level that can be magnified into unexpected macroscopic behavior. New insights into interfacial processes are critically needed to enhance the rates of waste processing, predict the behavior of contaminants in waste streams and/or the subsurface environment, and effectively sequester contaminants in waste forms.

Chemical and Physical Processes at Interfaces

As described in the PRD, *Elucidating and Exploiting Complex Speciation and Reactivity Far from Equilibrium*, the fundamental basis for describing chemical speciation and reactivity in extreme chemical systems represented by typical EM problems is severely lacking. The full description of critical interfacial chemical and physical processes of relevant species found in bulk waste systems represents another major knowledge gap. At these interfaces, molecular structure is perturbed compared to the bulk system, leading to major changes in local molecular structure and reactivity. To adequately describe and predict chemical reactivity and solvent structure at such interfaces, physical phenomena involving electric double layers, hydrogen bonding, and other van der Waals forces must be considered.

At the nanometer scale and smaller, the behavior of water and other polar constituents at interfaces is different from that of bulk, unconstrained solvent molecules. As shown in Figure 8, at the interface of quartz (SiO_2) and aqueous solutions of 0.01M RbCl, a very strong densification of water at the interface is observed, relative to bulk water (Bellucci et al. 2015). The constrained solvent at the interface can lower energy barriers for transition states and reduce entropy barriers for reaction pathways, leading to unexpected reactions and macroscopic observations. In other cases, rare events can give rise to unexpected energy transitions that can drive surprising chemical effects. For example, recent work shown in Figure 9 elucidated the differences in solvent conformation and microsolvation of tributyl phosphate and its radiolytic products dibutyl and monobutyl phosphate at the n-hexane–water interface compared to the bulk solvent (Ghadar et al. 2015). Microsolvation is defined as the rare event where one solvent molecule temporarily penetrates the co-solvent phases and is fully solvated therein. From this work, tributyl, dibutyl, and monobutyl phosphates appear to exhibit a systematic increase in aqueous solubility and selectively partition to the interfacial region at the infinite dilution limit. The relationship between adopted configurations of the solute, orientation of the solvent, and the ability of the solute to enhance microsolvation, specifically the ability of n-hexane to penetrate the aqueous phase, has been demonstrated within a 20 Å radius of tributyl phosphate. These dynamics at the liquid-liquid interface provide insights into the nucleation and formation of interfacial solids as a result of radiolytic degradation of the tributyl phosphate.

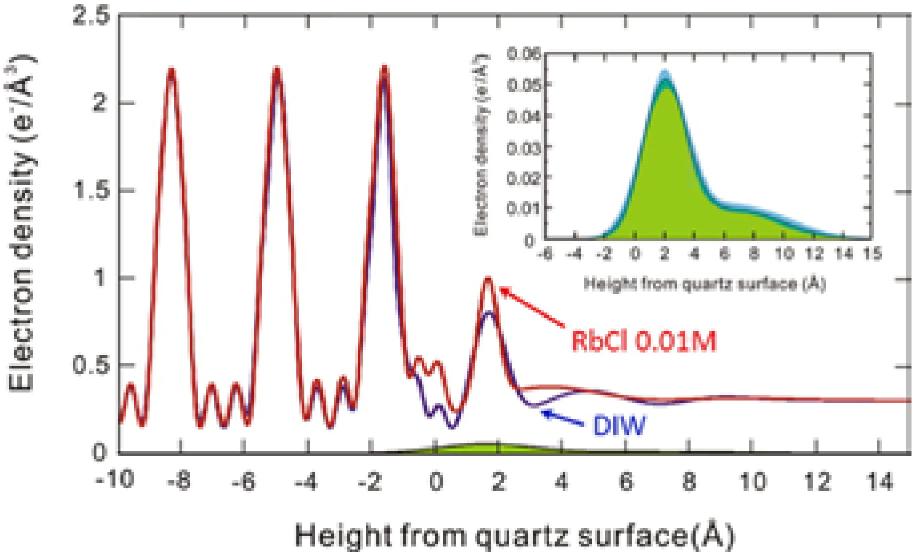


Figure 8. Electron density profile at the interface of quartz and pure water. The interface (at 0 Å) between quartz (SiO_2) on the left and aqueous solutions (pure water in blue, 0.01M RbCl in red) to the left from X-ray reflectometry conducted at the Advanced Photon Source at Argonne National Laboratory. Peaks locate structural positions of silicon and oxygen in quartz, and oxygen and rubidium in water at the interface, showing very strong densification of the interfacial water, relative to bulk water farther to the right. Insert from resonant anomalous X-ray scattering, shows that Rb^+ occurs in two structural sites, one within the dense interfacial water layer, and another farther from the surface (inner- vs. outer-sphere sorption). Reprinted with permission from Bellucci et al. (2015). Copyright 2015, American Chemical Society.

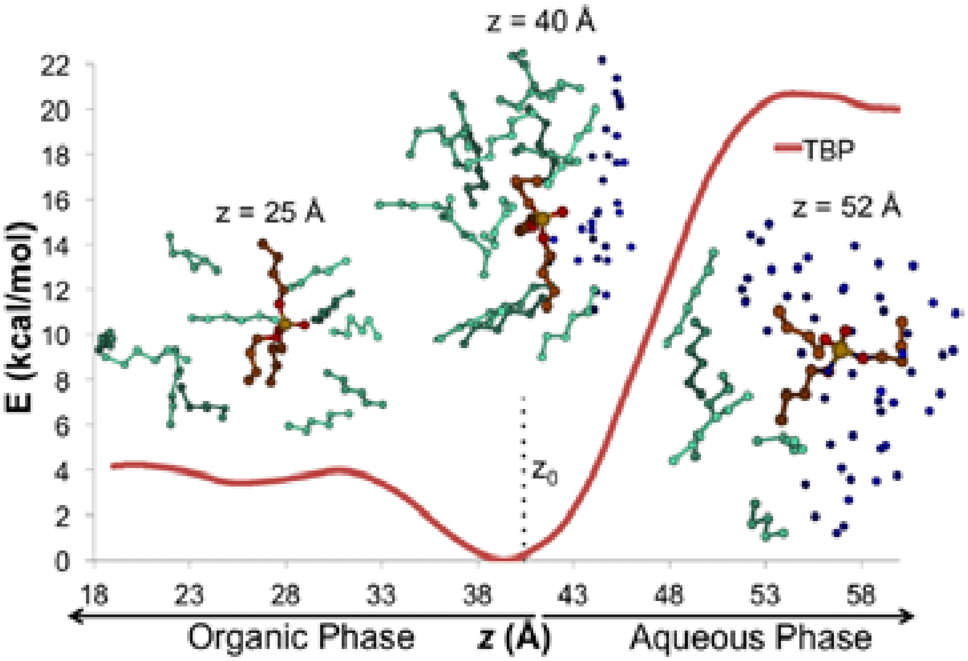


Figure 9. The organization of water molecules (small blue dots), n-hexane molecules (green alkane chains), and tributyl phosphate molecules (reddish-brown molecules) as a function of position across the liquid-liquid interface involving n-hexane and water. Note the energy minimum for the molecular structure shown at the liquid-liquid interface. Interestingly, this work also suggests transfer of small quantities of n-hexane into the aqueous phase with the tributyl phosphate molecule (although an energy barrier exists, as shown), and little water mixing into the n-hexane phase. Reprinted with permission from Ghadar et al. (2015). Copyright 2015, AIP Publishing LLC.

While some insight on interfacial phenomena has been gained over the past decade, the extremes in electrolyte concentration, pH, and high radiation fields lend a new dimension of complexity to this critically important topic. For example, much of our understanding of solvent radiolysis is derived from basic research conducted in bulk water. However, with limited water available, the quantity of solvent-derived radiolysis products and the overall reactivity of the system are expected to be quite different. New insight into the chemical and physical processes that occur at interfaces is critically needed to unlock new, highly efficient separation processes, devise effective environmental remediation strategies, and develop improved technologies for long-term waste storage.

Colloidal Behavior in the Environment and Rheological Behavior of Waste Stream Slurries

For many waste streams, including EM's high-level radioactive wastes, the levels of colloids can be quite high. The presence of these suspended particulates can lead to complex and unpredictable behaviors that can make the handling and processing of these waste streams exceptionally difficult. For example, the interactions of colloidal particles with solvent and with each other give rise to sometimes unexpected flow characteristics, and colloidal transport in subsurface groundwater systems has been implicated in surprising rates of contaminant migration from underground sources around the world (for example, Kersting et al. 1999; Novikov et al. 2006).

For Newtonian fluids, a linear relationship exists between shear stress and shear rate, with the coefficient of viscosity defining the dependence between these two variables. In simple colloidal systems (for example, monodisperse, charged spherical solids suspended in a dilute electrolyte), this coefficient of viscosity is a measure of the interactions between components of the slurry, which is reasonably described by the combination of attractive van der Waals forces and repulsive electrostatic forces. These interactions are described using Deryaguin-Landau-Verwey-Overbeek (DLVO) theory (Boström et al. 2001). For non-Newtonian fluids, the relation between shear stress and shear rate is not linear and can even be time dependent.

For complex slurries such as high-level radioactive waste, significant non-Newtonian behavior arises from the impact of concentrated electrolytes, which collapses the electrical double layer around the charged particle. This leads to the increased significance of van der Waals and other non-DLVO forces, which are largely undefined for the extreme conditions of typical EM waste streams. Basic research is needed to define the interfacial molecular reactions and their coupling to other forces across spatial scale. This improved understanding will provide the basis for controlling the rheology of the high-level radioactive wastes during processing, which will reduce operational liability associated with unwanted precipitation in process lines. It may also provide a foundation for developing technologies such as pipe coatings and waste stream additives that will inhibit coagulation and precipitation within the process lines.

Research Directions

Understanding and controlling interfacial chemical and physical processes are central to addressing EM mission needs. These interfacial processes can cause key radionuclides to be sequestered and impact availability in separation processes or even enhance transport in the subsurface. Interactions between particles can cause difficulties in fluid flow and lead to clogging of processing equipment. Building from the research directions focused on speciation and reactivity in complex, heterogeneous media outlined in the PRD, *Elucidating and Exploiting Complex Speciation and Reactivity Far from Equilibrium*, this PRD specifically focuses on the reactivity of the relevant species at interfaces. The research directions described here focus on the molecular level to the approximately micron scale and relatively short time domains (for example, typically minutes or less). The challenges associated with integrating these directions into larger spatial scales and longer temporal domains are addressed in the PRD, *Predictive Understanding of Subsurface System Behavior and Response to Perturbations*.

Understanding Interfacial Chemical Reactivity and Solvent Structure under Extreme Conditions

Considerable progress has been made in understanding liquid-solid interfacial processes; however, under extreme conditions encountered in EM wastes, such as concentrated electrolytes, high pH, and ionizing radiation, interfaces will evolve and interact with species in solutions in unexpected ways. For example, we know that solid phase structures, and therefore their chemical and physical characteristics, can be altered due to radiation-induced damage. But the ionizing radiation can also change the chemistry of the species expected in the system. As chemically diverse species in solution interact with irradiation-induced defects in the materials, new and unexpected phases can precipitate, which change the stability of the host structure. In addition, radioisotopes can be incorporated into the material and subsequently undergo radioactive decay. Radioactive decay transmutes the original element and isotope into different elements and isotopes, leading to an evolution of the material over time. These decay products may be less stable in the surrounding matrix than the original nuclides. This further complicates understanding these dynamic systems that are far from equilibrium.

Understanding the myriad chemical and physical processes and resulting structural and reactivity changes at the interfaces is a major knowledge gap. To address this gap, a full assessment of the complex, multicomponent, multiphase materials in waste systems is required. This would include, for example, understanding the aggregate thermodynamic behavior of multiphase composite materials, including the role of interfaces in stabilizing metastable phases. Physical forces are also important for understanding structure and reactivity at surfaces. For example, van der Waals forces are very important at interfaces. Although van der Waals interactions are weak, their influence at interfaces can dominate the overall behavior of the system. Van der Waals forces play a large role in solvent structure for polar solvents at the surfaces of charged particles, and recent work demonstrates that the water structuring near solid-liquid interfaces is highly correlated with van der Waals forces (Chun et al. 2015).

Elucidating these many chemical and physical processes requires new experimental approaches that must be integrated with computational calculations, models, and simulations that can extend across scales (see also *Transformative Research Capabilities*). For example, phase-diagram information from Computer Coupling of Phase Diagrams and Thermochemistry can be supplemented by ab initio data of possible metastable/nonequilibrium phases that might occur. Similarly, accelerated molecular dynamics and kinetic Monte Carlo methods can be used to assess kinetic pathways and their impact on the evolution of the material. A key need in this area is the development of high-quality charge-transfer potentials that can accurately account for the behavior of interfacial chemical species in a wide range of atomic environments, and in the presence of electronic and atomic defects, to serve as the foundation of atomistic modeling efforts.

Advances in spectroscopic and computational approaches over the past decade provide the capability to directly probe reactivity at surfaces such as acid-base reactions, solvent dynamics, and particle-particle interactions. For example, in Figure 10, experimental force data obtained with atomic force microscopy is compared directly with ion density profiles from molecular dynamics simulations providing a comprehensive picture of the electrical double layer structure for uncharged and charged highly ordered pyrolytic graphite in an ionic liquid electrolyte (Black et al. 2013). These types of combined characterization and computational studies are critically needed to enable the prediction of the nucleation, aggregation, and formation of interfaces in dynamic systems; the chemical forces that drive dissolution; and the transfer of molecular species across these interfaces. Further examples are outlined in the *Transformative Research Capabilities* section.

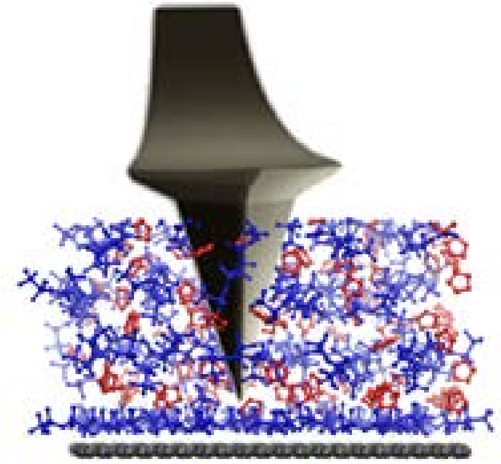


Figure 10. Schematic of an in situ investigation of an interface. Here, ionic liquids form an alternating structure of anion/cation layers at the solid-liquid interface. As an atomic force microscopy tip approaches the surface it detects forces as it moves through the dense ion layers (Black et al. 2013). Image courtesy of Oak Ridge National Laboratory.

Solvent Behavior in Confined, Nanoscale Environments

In many EM waste environments, the concentrations of water and other typical solvents relative to other components are generally quite limited. As a result, these species are often confined to nanoscale environments. This nanoconfinement could lead to unexpected behaviors. The basic knowledge for describing physicochemical reactions in such confined nano environments, in particular in the presence of ionizing radiation, is lacking.

Recent work has shown that the hydrogen bonding of confined water in concentrated electrolyte solutions can be quite different from that in bulk solutions (Corsaro et al. 2016). Similarly, water constrained in nano environments, such as carbon nanotubes, has been shown to exhibit markedly different hydrogen bonding behavior that can possibly be "tuned" by varying the electrostatics of the carbon nanotube environment via chemical functionalization (for example, Sahu and Ali 2015). Understanding the impact of ionizing radiation on confined water and other confined solvents is necessary for predicting and exploiting interfacial chemistry in high-level radioactive wastes.

As outlined in the *Transformative Research Capabilities* section, recent advances in analytical techniques are now making it possible to study interfacial processes and reveal unprecedented levels of information. In the case of electron microscopy, atomic-level spatial resolution is now possible and liquid stages are available to directly observe the solid-liquid interface. Similarly, hydrogen/deuterium exchange can be used with neutron scattering to investigate interactions of water and other solvents with minerals and other materials as well as reveal the movement of water through pores. Chemical imaging techniques have also been used to observe self-assembly of solvent molecule structures.

Linking Interfacial Reactivity with Macroscopic Properties

As a macroscopic property, waste stream rheology is an exceptionally challenging aspect of processing high-level radioactive waste streams, which often have consistencies that are similar to wet cement or peanut butter making them very difficult to move through process waste streams. These rheologies are driven by non-DLVO forces.

At the molecular level, non-DLVO forces are impacted by acid-base interactions, solvation forces, and steric and molecular bridging forces (Grasso et al. 2002). For highly concentrated electrolytes, such as the high-level radioactive waste, water structuring at particle-liquid interfaces and coupled van der Waals forces can lead to unique interactions that govern agglomerate structures and bulk rheology. Furthermore, for suspensions composed of differing solids species or with complex particle surface chemistries, differences in the surface charges and higher concentrations of multivalent ions can lead to unexpected phenomena, such as a reversal of forces and electrostatic attractions. These colloidal interactions can also lead to agglomeration and ultimately precipitation, which should be avoided when trying to process highly radioactive waste materials.

Recent studies have found that, contrary to DLVO theory predictions, agglomeration at high salt concentrations proceeds rapidly, leading to a "restabilization" of colloids with respect to aggregation at high salt (Huang and Berg 2006; Manciu and Ruckenstein 2004). High-salt restabilization is attributed to hydration forces that are generally believed to be correlated with water structuring in the vicinity of particle surfaces. The forces are dependent not only on the ionic strength, but also on type of ions. Ion specificity has been known to influence the interfacial chemistry of particles and colloidal stability (Boström et al. 2001; Das and Rohatgi 2010; dos Santos and Levin 2011; Peula-García et al. 2010). In fact, work focused on environmental systems (for example, groundwaters, low electrolyte systems) does not directly translate to tank waste systems (high electrolyte systems) because the non-DLVO interactions are quite different. These differences are manifested, for example, in the significant problems associated with tank waste rheology at the Hanford Waste Treatment and Immobilization Plant. Thus, fundamental understanding of these molecular-level phenomena may provide critical insight into these and other types of problematic macroscale behavior.

Advances in characterization techniques are needed to provide direct characterization of particle interactions in complex systems and greatly enhance the understanding of interactions among major waste components. For example, colloid-probe atomic force microscopy can measure short-range particle-

particle interaction forces in solution, with force resolution of 1–100 pN and spatial resolution of 0.5–2 nm. Further, this technique can be extended to measure friction and adhesion forces between particles. Advances in other types of imaging techniques, such as transmission electron microscopy and scanning electron microscopy, now allow particulates to be measured in solution. Similarly, small-angle X-ray and neutron scattering techniques are also capable of in situ studies of particle aggregates microstructure.

In addition to these advances in experimental tools, computational schemes and algorithms are needed to translate molecular phenomena to the mesoscale, and even to the system scale. For example, understanding the molecular phenomena that drive aggregation in suspensions and bulk rheologies is essential for mitigating the risks for pipe clogging during high-level radioactive waste processing. Capturing the relevant molecular processes accurately as phenomena are scaled up to macroscopic phenomena is essential for reflecting the dynamic nature of the chemical phenomena.

In summary, interfacial processes, both chemical and physical, impact virtually all aspects of EM’s mission. In processing wastes, interfacial interactions can decrease the recovery of harmful species from those that are benign and can cause particulates to aggregate and clog pipes. Interfacial interactions of radioactive species with both minerals and particulates in the subsurface can have a huge impact on the fate and transport of these species and impact remediation processes. Understanding these processes at the molecular level and extending this knowledge to the systems level is a critical first step in formulating new technologies for waste processing and environmental remediation.

Technology Impacts

The benefits of research on interfacial phenomena are far reaching within EM missions and will impact many other areas, including effective and efficient waste processing, geologic disposal, and environmental remediation strategies, as well as provide insight that will lead to vastly improved separations systems. For example, to support EM’s mission, it is critical to predict the performance of waste processing streams and the remediation of the subsurface environment. To develop these models requires detailed knowledge of a multitude of chemical and physical parameters, including spatial distributions, types, and amounts of the many components present that impact key interfacial processes. Armed with this knowledge of the interfacial chemistry and physics in heterogeneous systems, high-fidelity models can be established. These improvements will open up new, highly reliable, and predicable waste processing and environmental remediation strategies.

This knowledge would also allow tank waste behaviors, including agglomeration, precipitation, rheology, and filtration, to be predicted and altered to control and optimize tank waste processing and environmental remediation. For example, the primary limitation for both the Hanford and Savannah River Sites’ treatment schemes for high-level waste sludge is associated with the rheological properties of wastes, which can range by several orders of magnitude at a given solids concentration. Fundamental understanding of these properties would significantly expand the operational window for the waste treatment systems, thereby dramatically accelerating the waste treatment process.

References

Bellucci F, SS Lee, P Fenter, JD Kubicki, A Bandura, Z Zhang, and DJ Wesolowski. 2015. “Rb^+ Adsorption at the Quartz(101)–Aqueous Interface: Comparison of Resonant Anomalous X-Ray Reflectivity with ab Initio Calculations.” *Journal of Physical Chemistry C* 119(9): 4778–4788. DOI: 10.1021/jp510139t.

Black JM, D Walters, A Labuda, G Feng, PC Hillesheim, S Dai, PT Cummings, SV Kalinin, R Proksch, and N. Balke. 2013. "Bias-Dependent Molecular-Level Structure of Electrical Double Layer in Ionic Liquid on Graphite." *Nano Letters* 13(12): 5954–5960. DOI: 10.1021/nl4031083.

Boström M, DRM Williams, and BW Ninham. 2001. "Specific Ion Effects: Why DLVO Theory Fails for Biology and Colloid Systems." *Physical Review Letters* 87(16): 168103. DOI: 10.1103/PhysRevLett.87.168103.

Chun J, CJ Mundy, and GK Schenter. 2015. "The Role of Solvent Heterogeneity in Determining the Dispersion Interaction between Nanoassemblies." *Journal of Physical Chemistry B* 119(18): 5873–5881. DOI: 10.1021/jp512550c.

Corsaro C, D Mallamace, N Cicero, S Vasi, G Dugo, and F Mallamace. 2016. "Dynamics of Water Clusters in Solution with LiCl." *Physica A: Statistical Mechanics and its Applications* 442: 261–267. DOI: 10.1016/j.physa.2015.09.008.

Das A and A Rohatgi. 2010. "Optical and Electrical Characterization of Silver Microflake Colloid Films." *Journal of Electrochemical Society* 157(3): H301–H303. DOI: 10.1149/1.3276456.

dos Santos AP and Y Levin. 2011. "Ion Specificity and the Theory of Stability of Colloidal Suspensions." *Physical Review Letters* 106(16): 167801. DOI: 10.1103/PhysRevLett.106.167801.

Ghadar Y, P Parmar, A Samuels, and AE Clark. 2015. "Solutes at the Liquid-Liquid Phase Boundary – Solubility and Solvent Conformational Response Alter Interfacial Microsolvation." *Journal of Chemical Physics* 142(10): 104707. DOI: 10.1063/1.4914142.

Grasso D, K Subramaniam, M Butkus, K Strevett, and J Bergendahl. 2002. "A Review of Non-DLVO Interactions in Environmental Colloidal Systems." *Reviews in Environmental Science and Biotechnology* 1(1): 17–38. DOI: 10.1023/A:1015146710500.

Huang AY and JC Berg. 2006. "High-Salt Stabilization of Laponite Clay Particles." *Journal of Colloid and Interface Science* 296(1): 159–164. DOI: 10.1016/j.jcis.2005.08.068.

Kersting AB. 2013."Plutonium Transport in the Environment." *Inorganic Chemistry* 52: 3533−3546. DOI: 10.1021/ic3018908.

Kersting AB, DW Efurd, DL Finnegan, DJ Rokop, DK Smith, and JL Thompson. 1999. "Migration of Plutonium in Ground Water at the Nevada Test Site." *Nature* 397(6714): 56–59. DOI: 10.1038/16231.

Manciu M and E Ruckenstein. 2004. "The Polarization Model for Hydration/Double Layer Interactions: The Role of the Electrolyte Ions." *Advances in Colloid and Interface Science* 112(1–3): 109–128. DOI: 10.1016/j.cis.2004.09.001.

Novikov AP, SN Kalmykov, S Utsunomiya, RC Ewing, F Horreard, A Merkulov, SB Clark, VV Tkachev, and BF Myasoedov. 2006. "Colloid Transport of Plutonium in the Far-Field of the Mayak Production Association, Russia." *Science* 314(5799): 638–641. DOI: 10.1126/science.1131307.

Peula-García JM, JL Ortega-Vinuesa, and D Bastos-Gonzalez. 2010. "Inversion of Hofmeister Series by Changing the Surface of Colloidal Particles from Hydrophobic to Hydrophilic." *Journal of Physical Chemistry C* 114(25): 11133–11139. DOI: 10.1021/jp912035v.

Powell BA, Z Dai, M Zavarin, P Zhao, and AB Kersting. 2011. "Stabilization of Plutonium Nano-Colloids by Epitaxial Distortion on Mineral Surfaces." *Environmental Science and Technology* 45: 2698–2703. DOI: 10.1021/es1033487.

Russel RL, RA Peterson, HD Smith, DE Rinehart, PM Aker, and EC Buck. 2009. *Development and Characterization of Boehmite Component Simulant.* PNNL-18176, Pacific Northwest National Laboratory, Richland, Washington.

Sahu P and SM Ali. 2015. "The Entropic Forces and Dynamic Integrity of Single File Water in Hydrophobic Nanotube Confinements." *Journal of Chemical Physics* 143(18): 184503. DOI: 10.1063/1.4935373.

Snow LA, RC Daniel, LK Jagoda, RA Peterson, EC Buck, KE Draper, ED Jenson, RG Swoboda, AJ Casella, MK Edwards, AE Kozelisky, JV Crum, SK Fiskum, and PJ MacFarlan. 2009. "Characterization and Leach Testing for PUREX Cladding Waste Sludge (Group 3) and REDOX Cladding Waste Sludge (Group 4) Actual Waste Sample Composites." PNNL-18054, WTP-RPT-167, Rev. 0, Pacific Northwest National Laboratory, Richland, Washington. http://www.pnl.gov/main/publications/external/technical_reports/PNNL-18054.pdf.

HARNESSING PHYSICAL AND CHEMICAL PROCESSES TO REVOLUTIONIZE SEPARATIONS

Abstract

There are few challenges within the field of separations science that match those posed by EM tank wastes. These challenges are due to the highly heterogeneous and dynamic nature of these wastes as well as their extreme environments, including high pH, ionic strength, and radiation. The extreme condition of these wastes places an urgent demand for the development of robust and well-understood technologies to enable safe, selective, efficient, and cost-effective cleanup of wastes. New strategies for isolating risk-driving radionuclides and other toxic constituents from complex waste mixtures require fundamental understanding of molecular-level chemical and physical processes that can be deliberately and rationally manipulated to optimize the selective separations of targeted species. This knowledge will enable the design of a new generation of molecules and materials capable of providing revolutionary advances in separations technologies to fulfill EM mission needs.

Scientific Challenges

Separations processes are designed to partition a mixture of materials into its various components. Large-scale separations processes are used daily in multibillion dollar petroleum, mining, chemical, and pharmaceutical industries for production of commercial products. In addition, smaller scale separations processes are used for the analysis of components in medical, environmental, forensic, and other applications. The field of separations science encompasses a wide range of fundamental scientific concepts based on coordination, inorganic, and physical chemistries as well as colloid, soft matter, and interfacial sciences. Separations processes may be described thermodynamically in terms of chemical potential gradients within dynamic systems that may also be perturbed by imposing external stimuli, such as electrical, magnetic, gravitational, or radiation fields. The enabling concept that resides at the crux of separations science is selectivity. To control selectivity, one draws from many branches of chemistry and physics to understand the origin of differences in the properties of species in mixtures and learns how to manipulate the driving forces and time-dependent constraints that act on these properties. Thus, separations science is driven by properties of species, matrix interactions, and the nature of useful chemical transformations.

More than 70 years have elapsed since initial operation of the first industrial-scale radioactive separations process for the recovery of plutonium. These initial processes, such as the PUREX process, which uses tributyl phosphate to selectively partition plutonium(IV) and uranium(VI) from the other solutes in the aqueous phase (see Appendix A for further details), originated from a base of fundamental scientific knowledge, which then proceeded through applied research, followed by an engineering stage leading to plant operation. Since then, the approaches used for separations of these complex radioactive mixtures have been modified and optimized but in their essence have not progressed significantly. Many changes that have been implemented are incremental, involving either lengthy trial-and-error approaches or engineering "work-arounds." Other changes resulted from system-specific fundamental information developed over the decades. While the incremental changes allowed by applied research supported by increasing fundamental knowledge have been extremely valuable, the recalcitrance of tributyl-phosphate-based chemistry, such as found in PUREX, to supplanting alternative technology stands as a sign of the magnitude of innovation required. While the problems of PUREX are well known, implementation of an alternative technology will require a paradigm shift. In the same respect, the nature of EM problems can be seen to pose similar challenges to separations science and technology.

One important example of the impact of fundamental science on waste separations is the next-generation CSSX process (Moyer et al. 2005; Pierce et al. 2012). Before the development of CSSX, very high sodium concentrations found in waste tanks severely interfered with the separation of ^{137}Cs in high-level wastes at the Savannah River Site. The CSSX process solved this dilemma using a novel, highly selective chelating agent (BOBCalixC6 extractant) that was developed based on over a decade of fundamental research on macrocyclic extractants in projects funded by the DOE Office of Science Basic Energy Sciences. This process has been successfully deployed at scale at the Savannah River Site to remediate millions of liters of wastes. This is an outstanding example of how basic research can provide new insights to tackle what previously had been viewed as a nearly insurmountable problem that would require additional costly and time-consuming separations steps.

Another example is illustrated by the persistent formation of third phases. During decades of PUREX process operations the world over, plant operators learned empirically to avoid conditions that promoted third-phase formation, some of which could pose serious safety risks, including criticality, in radioactive systems. Recently, in studies using Office of Science neutron and X-ray user facilities, the fundamental basis for the formation of this third phase was revealed to arise from the self-assembly of molecular species into nanoscale aggregates and subsequent assembly of aggregates into meso-ordered structures (Testard et al. 2010).

EM's wastes represent some of the most challenging mixtures on Earth, which are made even more complicated by extremes in radiation and high pH and ionic strengths. Contaminated environmental systems such as groundwater present other challenges of extreme dilution and the presence of myriad mineralogical and biological effects. Today's separations technologies fall far short of meeting the remediation challenges faced by EM. These technology gaps can only be addressed by gaining fundamental insight into the physical and chemical processes that can be harnessed to effect efficient, cost-effective separations of EM's hazardous wastes.

Research Directions

Revolutionary approaches are needed to address the daunting separations challenges required to meet the requirements of the EM mission. A critical first step is to understand the behavior of the specific chemical species to be separated, in this case specific radionuclides and their fission products, as outlined in the PRD, *Elucidating and Exploiting Complex Speciation and Reactivity Far from Equilibrium.* In addition to identifying the full range of species present in the extreme conditions engendered in EM wastes, the numerous chemical and physical processes (including reduction-oxidation, complexation, and precipitation, among others), which occur in these nonequilibrium environments, need to be understood to facilitate the design of highly selective and efficient separations approaches. The following key research directions have been identified to both elucidate and exploit fundamental processes required to design molecules and materials for next-generation separations processes for EM wastes.

Understanding Mechanisms that Drive Separations at Interfaces

Separations processes involve mass transport at or across interfaces: liquid-liquid, solid-liquid, gas-liquid, or other combinations. Therefore, understanding and controlling chemical (for example, coordination chemistry, bond covalency, and ligand design) and physical processes (for example, mass, charge, dielectric constant, and magnetic response) that occur at interfaces is a key to developing atom-efficient separations schemes. Interfacial thickness in most separations systems is on the order of 10 nm, while bulk-phase dimensions in typical multiphase systems may be on the order of 100 μm; thus, all mass transport is controlled by only 1/10,000 of the volume of a typical separations system. As the effective "gatekeeper," the interface is responsible for separations rate, which translates to throughput, plant footprint, and overall economic viability. Understanding this rate-controlling role is thus critical for the design of effective separations systems.

However, the interfacial role extends far beyond kinetics. Interfaces are generally not static, but rather form, disappear, and move in space, as in crystallization or dissolution processes. In liquid-liquid systems, the interface is repeatedly formed and broken in mixing and coalescence. Such dynamic phenomena are often overlooked, but they are as integral to the design of a separations agent as is its binding selectivity. A related overlooked interfacial problem is fouling. All real-world separations systems degrade by some form of fouling whose origin is an interfacial effect that was not foreseen in the concept design. While this problem is usually handed to the engineers, it can spell ultimate rejection of an otherwise elegant chemical system and therefore merits fundamental inquiry. Finally, interfacial properties can be critical for separations selectivity. While bulk-phase properties are typically tailored to obtain the desired selectivity, the gatekeeping role of the interface represents an open opportunity to enhance selectivity employing only a microscopic fraction of the overall system volume. In summary, it may be seen that controlling the properties of phase interfaces in separations systems offers a vast opportunity to not only enhance efficiency and selectivity in existing types of systems, but to develop entirely new separations with unprecedented economic potential.

Understanding these interfacial processes requires a variety of analytical techniques, as outlined in the *Transformative Research Capabilities* section. Indeed, new X-ray and neutron scattering and spectroscopic techniques represent a breakthrough in understanding interfacial properties, kick starting research that had long since stalled using classical methodology. Many state-of-the-art techniques now allow these interfaces to be examined in situ, including X-ray and neutron scattering and spectroscopy (including small-angle and wide-angle techniques), optical probes (such as second harmonic generation), and various microscopies (including electron, scanning probe, and optical modalities). However, new types of characterization technologies are needed to probe the full range of interfacial processes across multiple spatial and temporal scales that will be required to fully understand these complex processes. Because tank waste samples have high radionuclide content, microfluidics techniques can aid in handling small samples, especially when coupled with a variety of characterization techniques (Nichols et al. 2011).

Design and Synthesis of Molecular and Materials Architectures with Tailored Properties

The success of highly selective chemistry such as CSSX validates the power of molecular recognition in EM applications, but made-to-order selectivity is not yet a reality and remains a major challenge. While Nobelists Lehn and Cram long ago delineated the core principles of molecular recognition, a fundamental lack of knowledge in the science underlying the design of new materials has stalled progress. Two criteria for separations materials of the future include high selectivity and efficient binding-release cycling. Regarding selectivity, EM wastes require high separations factors owing to the dilute nature of contaminants in streams containing relatively high concentrations of competing species. Ideally, these separations must also exhibit this selectivity in rapid mass-transport systems while consuming a minimum of energy and producing no secondary waste. Inherent selectivity reduces the footprint of a facility as well as the amount of material required and as such offsets the cost of expensive separations agents. However, today's capabilities in receptor chemistry fall far short of the selectivity needed for EM wastes.

When considering approaches to improve selectivity, a number of system-wide factors must be considered. For example, the structure in Figure 11 illustrates an approach for efficiently removing sulfate from EM wastes, which interfere with waste vitrification (Custelcean et al. 2008). Further, EM wastes typically require removal of multiple contaminants, and thus selectivity ideally implies simultaneous recognition of target species. Regarding the binding-release criterion, most designed receptors for target contaminants must also exhibit efficient release of the contaminants into a stream that can be used directly by downstream processes. In some cases, approaches using separations agents that can either be destroyed or converted into waste forms may be viable; however, to be most efficient, recycling the separations media may be desirable. For example, the economics of most molecular-recognition systems require that the separations agent be recovered and recycled thousands of times. Along with high selectivity and efficient binding-release cycling, interfacial properties and other characteristics such as high stability must be considered. Overall, the functional requirements of a designer separations material impose daunting challenges and opportunities for research of potential benefit to EM problems.

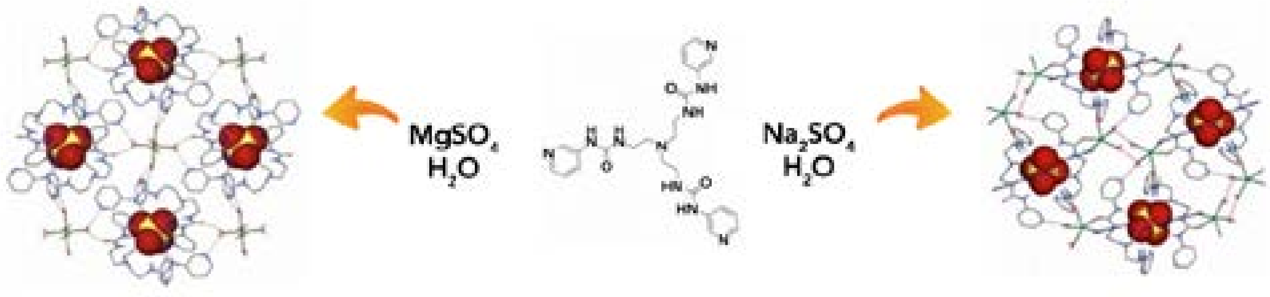


Figure 11. Aqueous sulfate separation by crystallization of urea-functionalized capsules. Each sulfate is completely encapsulated by an ideal 12 hydrogen bonds from three urea groups in each of two capsule-forming tripodal receptors. The capsules form insoluble crystals with alkali or alkaline earth metals, which is potentially useful for removing sulfate from wastes. Sulfate interferes with waste vitrification and its removal could reduce the amount of glass waste forms needed with large net savings in schedule and dollars. Modified by permission from John Wiley and Sons: Wiley Online Library, Custelcean et al. (2008). Copyright 2008.

Advances in nanoscience over the past decade—including synthesis, characterization, and computational modeling and simulation—have given rise to the ability to design and synthesize materials with specific architectures and even chemical functionalities at the nanoscale. These advances have already led to new separations materials and processes using liquid polymers, graphene, zeolites, and mesoporous carbons and other materials (Liang et al. 2008). For example, the design of nanoporous sorbents (Carboni et al. 2013a; Gorka et al. 2013; Gunathilake et al. 2015; Johnson et al. 2012) and new nanomaterials—especially graphene with its remarkable resistance towards radiolytic damage—can be tailored into novel structures for separations. This is demonstrated in Figure 12, which shows a remarkable new class of graphene thin films with crown ether moieties. These films have been demonstrated for selective alkali metal cation binding (Guo et al. 2014).

Manipulation of chemical properties or material dimensionalities opens the door to development of exciting new classes of new molecules and materials architectures that could be incorporated into separations schemes. For example, multiple functionalities could be designed into a single molecule or material to allow separations of multiple targeted species in a single step and thus simplify separations schemes. Further, it may be possible to devise materials that can adapt to different species or regenerate with a change of solvent or applied field. One can imagine, for instance, designing a chelating molecule that releases a captured cation with the application of a magnetic or electric field (in case of carbon-based nanoporous materials), allowing the chelator to be readily recycled for another round of separations.

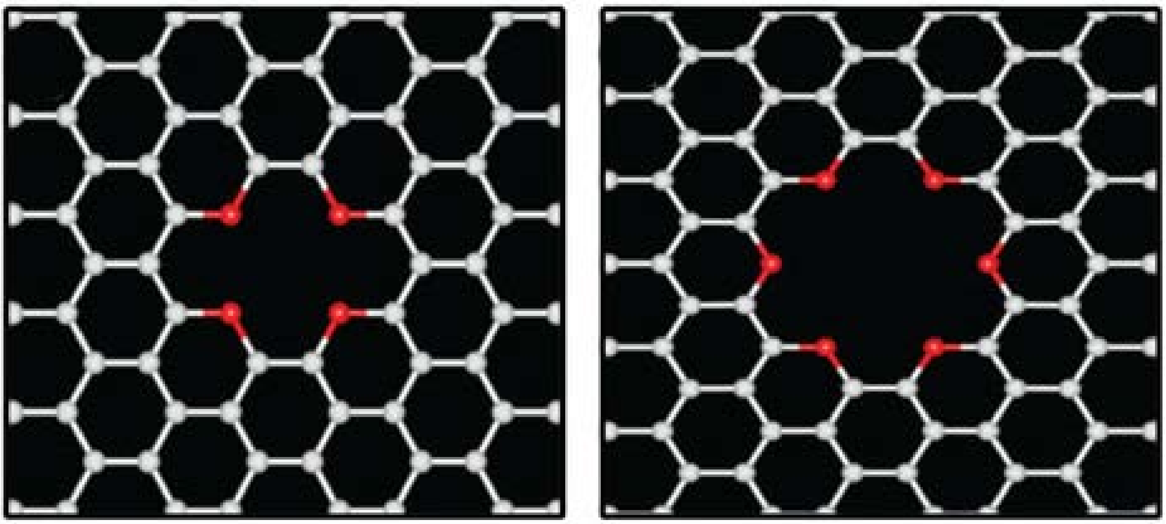


Figure 12. New class of graphene thin films for selective alkali metal cation binding. Reprinted by permission from Macmillan Publishers Ltd: *Nature Communications*, Guo et al. (2014). Copyright 2014.

Nanoporous materials based on metal-organic frameworks and porous organic polymers offer new possibilities to tailor the adsorption sites with high precision in combination with computational modeling. For example, a cooperative binding site with uranyl ions was created through a convergent orientation of functional groups at appropriate distances inside a metal-organic frameworkcavity (Carboni et al. 2013b). These cooperative sites give rise to a considerably enhanced selectivity for the targeted metal ions. By combining advanced polymer grafting techniques with nanoporous materials, high concentrations of functional groups can be grafted on these porous architectures (Yue et al. 2013).

New Approaches for Separations Based on Physical Properties and Chemical Properties

Separations approaches typically maximize the small differences between chemical and physical properties of targeted species to affect efficient separations. Current separations techniques for EM wastes have been used for decades with little innovation; however, there are many types of separations approaches that have not been applied to the types of materials found in EM wastes. For example, rare interactions/oxidation states might be manipulated to affect efficient separations (Runde and Mincher 2011). In this regard, it is well known that highly caustic electrolytes can stabilize high and otherwise unstable valence states, such as neptunium(VII), plutonium(VII), and americium(VII). These new chemical states could be exploited for separations processes using new and highly specific molecules and materials.

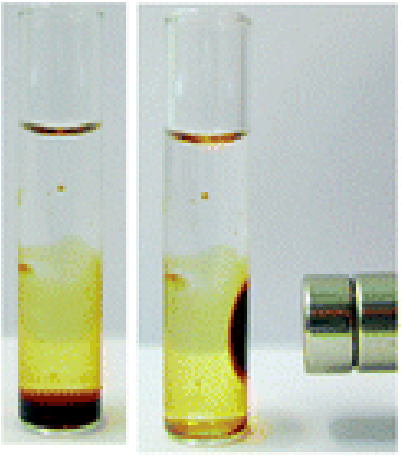


Figure 13. Magnetically responsive ionic liquids are an example of a new separations material. Reproduced in part from Branco et al. (2011) with permission of The Royal Society of Chemistry.

The success of future advanced remediation processes rests heavily on the creation of separations schemes capable of separating radionuclides with greater specificity and efficiency than ever achieved before. A prevailing issue is the development of active and functional solvent systems that can go beyond the current passive use of volatile organic solvents in liquid-liquid extraction. Ionic liquids are an emerging class of functional solvents (Sun et al. 2012). Compared with traditional organic solvents, ionic liquids offer many distinct advantages, such as negligible vapor pressures, good thermal stability, high ionic conductivity, broad electrochemical potential windows, and high synthetic flexibility as good solvents for a broad spectrum of inorganic and organic molecules. The unique ionic solvation environment can be potentially exploited in achieving high extraction efficiency and ion selectivity. Both solvent extraction and electroseparations can possibly be coupled to develop hyphenated separations systems based on ionic liquids. Figure 13 shows a magnetically responsive material based on ionic liquids that has the potential for the separations of solid wastes in stratified slurries found in EM waste tanks (Branco et al. 2011; Bwambok et al. 2013).

Finally, adaptive separations that take inspiration from biology could be imagined, wherein large-scale, self-recognizing, self-assembling, and self-healing processes drive solute partitioning in an incremental step-wise fashion. Stimulus-responsive separations based on physical properties, such as photochemistry, electrochemistry, magnetochemistry, or other phenomena, could also be imagined. This and many other physical and chemical properties of molecules could be exploited to yield a new generation of efficient separations technologies.

Technology Impacts

It is clear that to meet EM mission goals, a new generation of efficient and selective separations methods are overwhelmingly needed. The first critical step towards meeting this goal is to understand, predict, and eventually control chemical and physical processes to allow effective separations processes to be devised. Because interfaces control separations processes, understanding the processes that occur at liquid-liquid, liquid-solid, and other interfaces is also vital to this goal. Armed with this information, whole new classes of molecules and materials can be developed, leading to revolutionary separations technologies that have both high efficiency and high selectivity for the targeted species. Recent advances in nanoscience, which allow materials to be tailored to specific architectures and/or modified chemically to have specific functionalities, present a particularly exciting avenue for tailoring selectivity for EM waste separations. These nanoscience advances may also provide materials that are adaptive and self-restoring, adding even more value to the EM mission. New capabilities developed as part of this PRD will have far-reaching impact in other energy technologies where separations are critical, such as carbon dioxide reduction and biofuel production, as well as a broad range of industrial applications, such as chemical, pharmaceutical, and petroleum production.

References

Branco A, LC Branco, and F Pina. 2011. “Electrochromic and Magnetic Ionic Liquids.” *Chemical Communications* 47: 2300–2302. DOI: 10.1039/C0CC03892J.

Bwambok DK, MM Thuo, MBJ Atkinson, KA Mirica, ND Shapiro, and GM Whitesides. 2013. “Paramagnetic Ionic Liquids for Measurements of Density Using Magnetic Levitation.” *Analytical Chemistry* 85(17): 8442–8447. DOI: 10.1021/ac401899u.

Carboni M, CW Abney, SB Liu, and WB Lin. 2013a. “Highly Porous and Stable Metal-Organic Frameworks for Uranium Extraction.” *Chemical Science* 4: 2396–2402. DOI: 10.1039/C3SC50230A.

Carboni M, CW Abney, KML Taylor-Pashow, JL Vivero-Escoto, and WB Lin. 2013b. “Uranium Sorption with Functionalized Mesoporous Carbon Materials.” *Industrial & Engineering Chemistry Research* 52(43): 15187–15197. DOI: 10.1021/ie402646r.

Custelcean R, P Remy, PV Bonnesen, DE Jiang, BA Moyer. 2008. “Sulfate Recognition by Persistent Crystalline Capsules with Rigidified Hydrogen Bonding Cavities.” *Angewandte Chemie* 47(10): 1866–1870. DOI: 10.1002/anie.200704937.

Gorka J, RT Mayes, L Baggetto, GM Veith, and S Dai. 2013. “Sonochemical Functionalization of Mesoporous Carbon for Uranium Extraction from Seawater.” *Journal of Materials Chemistry A* 1(9): 3016–3026. DOI: 10.1039/C2TA01008A.

Gunathilake C, J Gorka, S Dai, and M Jaroniec. 2015. “Amidoxime-Modified Mesoporous Silica for Uranium Adsorption under Seawater Conditions.” *Journal of Materials Chemistry A* 3(21): 11650–11659. DOI: 10.1039/C5TA02863A.

Guo J, J Lee, CI Contescu, NC Gallego, ST Pantelides, SJ Pennycook, BA Moyer, and MF Chisholm. 2014. “Crown Ethers in Graphene.” *Nature Communications* 5: 5389. DOI: 10.1038/ncomms6389.

Johnson BE, PH Santschi, C-Y Chuang, S Otosaka, RS Addleman, M Douglas, RD Rutledge, W Chouyyok, JD Davidson, GE Fryxell, and JM Schwantes. 2012. “Collection of Lanthanides and Actinides from Natural Waters with Conventional and Nanoporous Sorbents.” *Environmental Science & Technology* 46(20): 11251–11258. DOI: 10.1021/es204192r.

Liang CD, ZJ Li, and S Dai. 2008. “Mesoporous Carbon Materials: Synthesis and Modification.” *Angewandte Chemie International Edition* 47(20): 3696–3717. DOI: 10.1002/anie.200702046.

Moyer BA, JF Birdwell Jr., PV Bonnesen, and LH Delmau. 2005. “Use of Macrocycles in Nuclear-Waste Cleanup: A Real-World Application of a Calixcrown in Technology for the Separation of Cesium.” In *Macrocyclic Chemistry: Current Trends and Future*, ed. K Gloe, Springer: Dordrecht, pp 383–405.

Nichols KP, RR Pompan, L Li, AV Gelis, RF Ismagilov. 2011. “Toward Mechanistic Understanding of Nuclear Reprocessing Chemistries by Quantifying Lanthanide Solvent Extraction Kinetics via Microfluidics with Constant Interfacial Area an Rapid Mixing.” *Journal of the American Chemical Society* 133(39): 15721–15729. DOI: 10.1021/ja206020u.

Pierce R, T Peters, T Caldwell, M Crowder, S Fink. 2012. “Performance Testing of the Next-Generation CSSX Solvent with Actual SRS Tank Waste, Separation Science and Technology.” 47(14–15): 2088–2097 Special Issue: *Seventeenth Symposium on Separation Science and Technology for Energy Applications*.

Runde WH and BJ Mincher. 2011. “Higher Oxidation States of Americium: Preparation, Characterization and Use for Separations.” *Chemical Reviews* 111(0): 5723–5741. DOI: 10.1021/cr100181f.

Sun XQ, HM Luo, and S Dai. 2012. “Ionic Liquids-Based Extraction: A Promising Strategy for the Advanced Nuclear Fuel Cycle.” *Chemical Reviews* 112(4): 2100–2128. DOI: 10.1021/cr200193x.

Testard F, T Zemb, P Bauduin, and L Berthon. 2010. “Third-Phase Formation in Liquid/Liquid Extraction: A Colloidal Approach.” In BA Moyer (ed.) *Ion Exchange and Solvent Extraction: A Series of Advances*, volume 19, CRC Press: Boca Raton, Florida, pp. 381–428.

Yue YF, RT Mayes, J Kim, PF Fulvio, XG Sun, C Tsouris, JH Chen, S Brown, S Dai. 2013. “Seawater Uranium Sorbents: Preparation from a Mesoporous Copolymer Initiator by Atom-Transfer Radical Polymerization.” *Angewandte Chemie International Edition* 52(50): 13458–13462. DOI: 10.1002/anie.201307825.

MECHANISMS OF MATERIALS DEGRADATION IN HARSH ENVIRONMENTS

Abstract

The degradation of structural materials, such as waste tanks, processing equipment, and radioactive waste storage systems, poses a huge threat to EM's mission. Materials exposed to harsh environments, including wastes containing high levels of radionuclides as well as extremes in pH and ionic strength, can degrade across broad timescales. These degradation rates may be very slow, such as for glass waste forms in a geologic repository, or may be relatively fast in an extreme environment, such as for bulk waste storage tanks. Material degradation in this PRD focuses on chemical reactions localized to interfaces of the material with its environment. The elementary and atomistic processes involved in these degradation processes are poorly understood. Fundamental knowledge of these processes is critical to develop new materials that can withstand the harsh conditions and ensure the long-term safety of waste handling and storage.

Scientific Challenges

Advances in understanding the fundamental mechanisms of materials property degradation in harsh, complex environments are a critical first step towards developing new materials to support EM's mission. Most studies of material failures have been conducted in a reactive mode, after a failure has occurred. New materials are needed that are less prone to failure and, importantly, predict eventual failures in systems that are expected to last for tens to thousands of years. Predictive modeling is needed to describe coupled reactive transport processes from nano- to mesoscale in complex harsh radiolytic environments from picoseconds to geologic timescales.

The ability to understand materials degradation and failure processes will significantly impact waste management and environmental remediation. The research directions outlined in this PRD seek to expand this understanding from the atomic to the systems level in a broad range of extreme environments, ranging from tank wastes to waste forms to spent nuclear fuel assemblies. Local environments can be probed by both experimental and computational methods, and the behavior of metals, glasses, and ceramics can be elucidated. A critical research component is validation of results. This includes validation of the modeling for prediction of speciation and interface behavior as well as for accelerated testing, which is required for the slow reactions associated with glass corrosion and passivation of metals.

Research Directions

Materials are central to EM's mission, including containment of stored materials processing equipment, such as pipes and valves, and waste storage systems including spent nuclear fuel assemblies, waste forms, and containment materials. The extreme conditions of the waste materials and their environments make access to these materials extremely difficult and failures of these materials translate into huge schedule delays and incurred costs. Thus, it is critical to develop new materials that can endure the extreme conditions of EM wastes. This will only be possible by understanding the underpinning fundamental chemical and physical processes by which materials are degraded. This PRD focuses on three research directions: fundamental radiation and electrochemical processes in complex systems, understanding corrosion mechanisms at the molecular level and in constricted volumes, and mechanisms of materials degradation in harsh environments.

Fundamental Radiation and Electrochemical Processes in Complex Systems

Because the material degradation processes are strongly dependent on the details of the local environment, it is critical to elucidate the chemistry of this environment and the influences of the ionizing radiation. Redox phenomena that are driven by electron, ion, and radical reactions stand at the core of chemistry for all elements on the periodic table. The presence of an ionizing radiation environment is the source of the production of an avalanche of secondary particles, the most important of which are low-energy electrons, solvated electrons, neutral radicals, radical ions, alpha and beta particles, neutrons, and gamma radiation.

The fundamental processes governed by both faradaic changes of oxidation state and non-faradaic changes (such as the cleavage of oxygen-hydrogen bonds in water that lead to radical formation) need to be elucidated. Further, the role of ionizing radiation on the formation and equilibria between nanoparticles, colloids, ultrafine precipitates, etc., as well as how it impacts the reactivity of a material's surface comprise an area that is poorly understood, yet critical to predict. For example, there is accumulating evidence to suggest that large metal-oxide clusters can enhance the effects of radiation chemistry (LaVerne 2005; Petrik et al. 2001; Poston et al. 2014). These multifaceted issues must be understood across many scales, from a simple hydrated ion (angstrom scale) to macromolecular grains (micron-scale colloidal systems) and beyond. Recent advances in characterization and computational techniques have the potential to provide insight into the radiochemical and electrochemical processes in complex tank fluids and waste form solid solutions. Of special importance are the capabilities available at DOE light sources, neutron sources, nanoscience research centers, and other user facilities that can provide insight into the fundamental chemistry and physics involved in these degradation processes. These capabilities are outlined in the *Transformative Research Capabilities* section.

Understanding Corrosion Mechanisms at the Molecular Level and in Constricted Volumes

Reactions of solid surfaces with their environments occur at interfaces and ultimately at the atomic level. For many forms of corrosion, the initial reactions take place in constricted or occluded regions in metals, glasses, and other materials that can develop gradients in the material's composition and electrochemical potential. In metals, the most aggressive forms of corrosion are local in nature such that the attack occurs primarily in pits, crevices, or cracks. The spatial separation of the anodic corrosion reaction within the occluded region from the cathodic reaction results in a locally concentrated electrolyte at the anodic site that is usually acidic owing to hydrolysis of cations. However, the very high, even saturated, concentrations of hydrated ions in these regions means that the concentration of water is very low, and the details of electrochemical reactions in such solutions are not well understood.

Occluded regions in glass are also critical in degradation processes. Reactions of water with glass result in a nanoporous hydrated silica material, dubbed the passivating reactive interphase. Water contacting and reacting with the unaltered glass must pass through the pores of the passivating reactive interphase for the corrosion process to proceed. Because of the nature of the size and surface chemistry of the pores, the chemistry and transport properties of the aqueous solution are significantly different than those of the bulk solution. Understanding the chemical and physical conditions within the confined media is critical to advance understanding of the mechanism of glass corrosion. For example, energy loss from inelastic X-ray scattering can provide insight to the bonding and chemical structure of the atoms in confined spaces and provide spectral fingerprints of constricted regions, such as pores in glass or pits in metals, and of the associated confined solutions. Further, quasielastic neutron scattering has recently been used to analyze water mobility in silica-based pore structures with varying chemistry and size (Figure 14). The results of these experiments can be used to confirm molecular dynamic simulations of water with various ions in contact with silica-based pore structures (Figure 15). The molecular dynamic calculations can then extend the experimental results to increasingly more realistic pore structures. Additional advances in characterization and modeling, as described in the *Transformative Research Capabilities* section, are needed to provide more information on these processes to fully understand the corrosive degradation of materials.

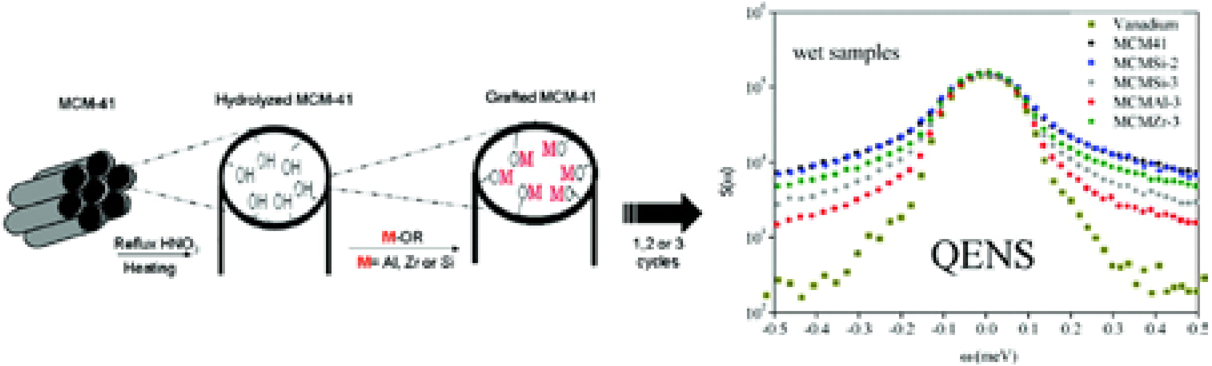


Figure 14. Quasielastic neutron scattering of functionalized nanopores. Reprinted with permission from Matar Briman et al. (2012). Copyright 2012, American Chemical Society.

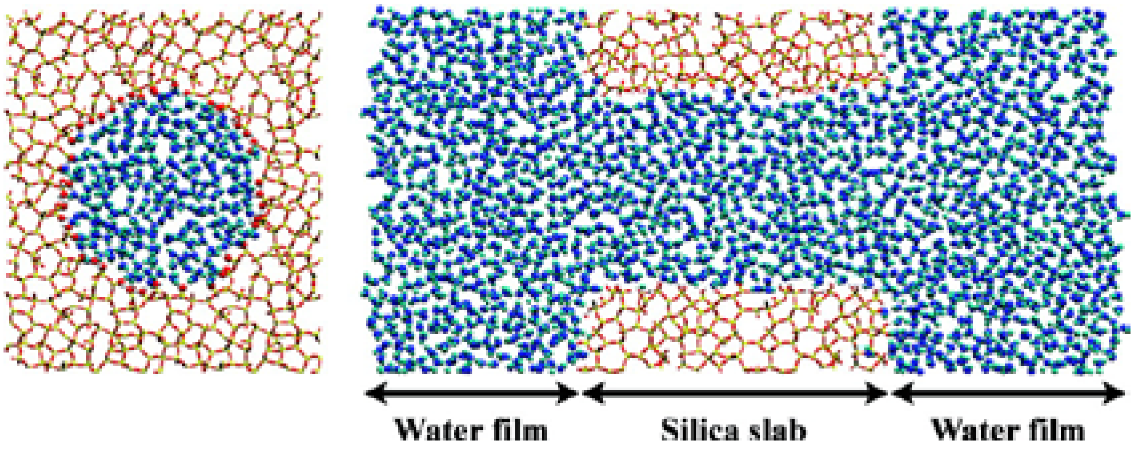


Figure 15. Molecular dynamic simulation of water diffusion through constricted SiO_2 glass nanopores. Adapted with permission from Bourg and Steefel (2012). Copyright 2012, American Chemical Society.

Advanced modeling methods are also needed to elucidate conditions in constricted environments. For example, density functional theory has been used to study the stabilization of single iron atoms in the nanopores of an ultrathin silica film grown on molybdenum(112), and the results were validated with scanning tunneling microscopy. The density functional theory results are shown in Figure 16, where the local densities of states for different configurations are given.

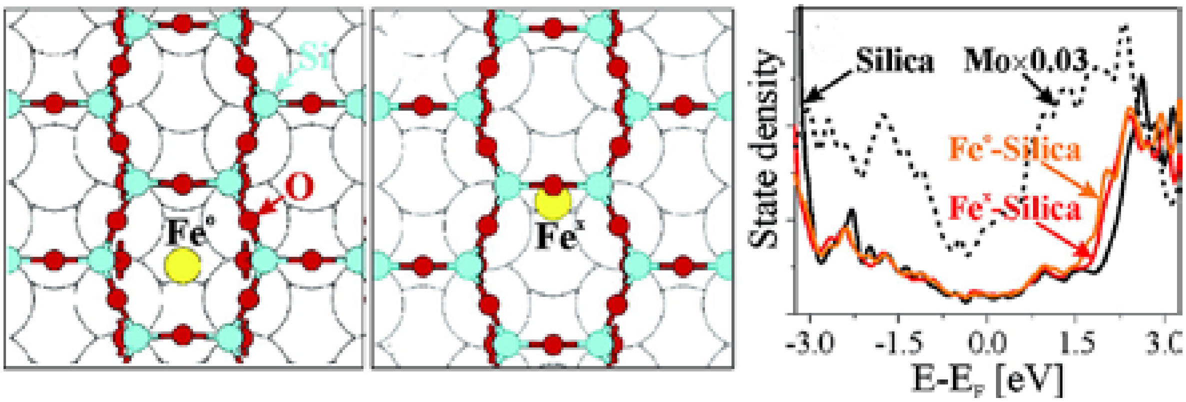


Figure 16. Results of a density functional theory calculation for iron atoms in two different binding sites at the silica/molybdenum(112) interface and the effect on the local density of states. Adapted with permission from Jerratsch et al. (2010). Copyright 2010, American Chemical Society.

Mechanisms of Materials Degradation in Harsh Environments

As stated previously, current knowledge of the full range of mechanisms that cause materials degradation in harsh environments is sorely lacking. Without this information, it will not be possible to design materials with the characteristics needed to meet the goals of EM's mission. The ability to gain this knowledge will be enabled by a new generation of characterization and computational tools that will allow detailed insight into these chemical and physical processes. Many of these areas are covered in the *Transformative Research Capabilities* section; however, examples specific to materials degradation are briefly described here.

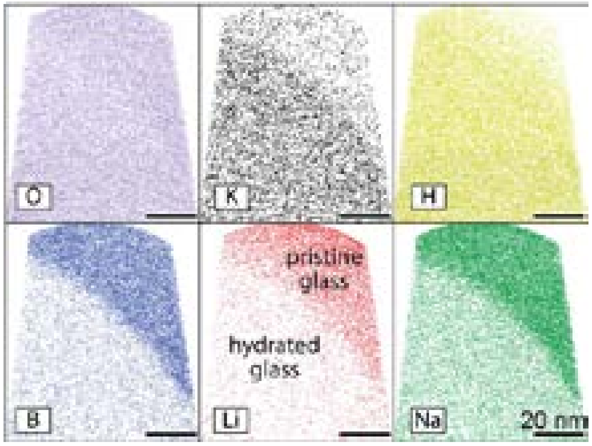


Figure 17. Atom probe tomography studies of waste glass corrosion front. Elements represented in each frame are identified at lower left corner. Reprinted from Gin et al. (2013). Copyright 2013, with permission from Elsevier.

Recent studies using atom probe tomography, a technique available at some of DOE's nanoscience research centers, have yielded composition of the reacting glass interface at an unprecedented resolution (Figure 17). In the figure, elemental distributions are shown in each frame for oxygen, potassium, hydrogen, boron, lithium, and sodium. The impact of corrosion on the distribution of the various elements is clearly evident.

Transformative modeling approaches must also be developed to provide the fundamental understanding of materials degradation processes. As described previously, atomistic modeling techniques, such as density functional theory, are now developing the ability to handle increasingly larger assemblies of atoms, adsorbed species, and even solvent water molecules. Such approaches will be essential to show how aggressive and inhibiting species interact with surfaces in solution. Figure 18 is an example of the results from a density functional theory calculation of a corroding interface. It shows a ternary alloy, represented by red, black, and gray balls, in an aqueous chloride (yellow balls) solution. The structure of the aqueous solvent and the locations of the adsorbed chloride ions are made evident in this image.

Some other modeling techniques required for the study of materials degradation are now emerging. For example, combined quantum/classical density functional theory has been used to account for short-range chemical forces and many-body electrostatic and electrodynamic forces driving the dissolution process. Seamless coupling of quantum and classical density functional theory approaches within a tightly coupled embedding multiscale framework has been demonstrated by Sushko et al. (2015) in modeling the oxidation of nickel alloys. These methods avoid the traditional shortfalls of both small cell size and difficult interpretation of kinetic data inherent in density functional theory and the challenge of defining force fields and representing true materials interactions inherent in molecular dynamics. It is clear the capability for modeling of materials degradation at interfaces is in its infancy, and advances in algorithms, coupled with high-performance computing that is available at DOE user facilities, should provide considerable insight into the structures and reaction pathways responsible for the degradation.

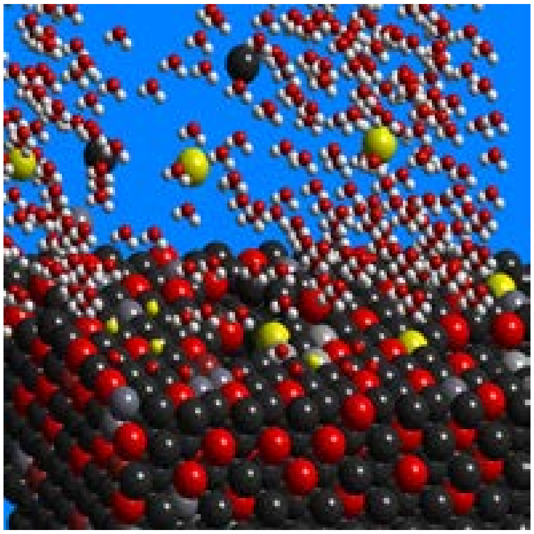


Figure 18. Results of a density functional theory calculation of a corroding interface of a ternary alloy, represented by larger red, black, and grey spheres, in an aqueous (hydrogen, small white; oxygen, small red) chloride (yellow) solution. The structure of the aqueous solvent and the locations of the adsorbed chloride ions are made evident in this image. Image courtesy of Taylor and Marcus (2015).

In summary, degradation of materials is a major concern for the remediation of waste sites due to the extreme environments and can result in substantial schedule delays and increased costs. The mechanisms of materials degradation, ranging from alloys found in waste tanks and waste processing equipment to glasses and ceramics used in waste forms, can vary widely depending on the specific environment of the materials; these mechanisms are currently poorly understood. Elucidating the fundamental chemical and physical processes responsible for materials degradation is a critical first step required to enable development of new materials. Fundamental studies are needed to understand radiation, chemical, and electrochemical processes at the molecular level and to scale these processes to the meso- and macroscales. This research will be enabled by development of new characterization tools capable of studying these materials under extreme conditions, combined with advanced modeling and simulation algorithms that allow these processes to be understood and predicted across scales of time and space.

Technology Impact

Environmental degradation of materials is a major concern for a wide range of technologies and applications related to virtually every sector of the economy, including energy generation, storage, and use; transportation; construction; and manufacturing. One of the greatest challenges to the safe and reliable use of materials is avoiding unanticipated failures. This need is especially acute in systems that are expected to last a long time (such as nuclear waste repositories) or systems for which operating life extensions are desired (for example, nuclear power reactors). Designing new materials that are less likely to fail and being able to reliably predict ultimate failure requires a comprehensive understanding of the fundamental chemical and physical processes that underlie materials failure. The research described in this PRD will enable development of a new generation of revolutionary materials to allow the safe containment of EM wastes and have immediate impacts on safe handling of other nuclear wastes and spent nuclear fuels. In addition, understanding corrosion mechanisms will support direct disposal of DOE-owned spent nuclear fuel and will allow for safe operation of the separations and vitrification plants at EM sites during the required plant lifecycle. Further, the information gained from this fundamental research will have a broad impact on a huge variety of other applications where robust materials are required.

References

Bourg IC and CI Steefel. 2012. “Molecular Dynamics Simulations of Water Structure and Diffusion in Silica Nanopores.” *Journal of Physical Chemistry C* 16(21): 11556–11564.

Gin S, JV Ryan, DK Schreiber, J Neeway, and M Cabie. 2013. “Contribution of Atom-Probe Tomography to a Better Understanding of Glass Alteration Mechanisms: Application to a Nuclear Glass Specimen Altered 25 Years in a Granitic Environment.” *Chemical Geology* 349–350: 99–109. DOI: 10.1016/j.chemgeo.2013.04.001.

Jerratsch JF, N Nilius, D Topwal, U Martinez, L Giordano, G Pacchioni, and HJ Freund. 2010. “Stabilizing Monomeric Iron Species in a Porous Silica/Mo(112) Film.” *ACS Nano* 4(2): 863–868. DOI: 10.1021/nn901609e.

LaVerne JA. 2005. “H_2 Formation from the Radiolysis of Liquid Water with Zirconia.” *Journal of Physical Chemistry B* 109: 5395−5397.

Matar Briman I, D RéBiscoul, O Diat, JM Zanotti, P Jollivet, P Barboux, and S Gin. 2012. “Impact of Pore Size and Pore Surface Composition on the Dynamics of Confined Water in Highly Ordered Porous Silica.” *Journal of Physical Chemistry C* 116:7021−7028. DOI: 10.1021/jp3001898.

Petrik NG, AB Alexandrov, and AI Vall. 2001. “Interfacial Energy Transfer During Gamma Radiolysis of Water on the Surface of ZrO_2, and some other Oxides.” *Journal of Physical Chemistry B* 105(25): 5935−5944. DOI: 10.1021/jp004440o.

Poston MJ, AB Aleksandrov, DE Sabo, Z Zhang, and TM Orlando. 2014. “UV Photon-Induced Water Decomposition on Zirconia Nanoparticles.” *Journal of Physical Chemistry C* 118: 12789-12795. DOI: 10.1021/jp501135r.

Sushko ML, V Alexandrov, DK Schreiber, KM Rosso, and SM Bruemmer. 2015. “Multiscale Model of Metal Alloy Oxidation at Grain Boundaries.” *Journal of Chemical Physics* 142(21): 214114. DOI: 10.1063/1.4921940.

Taylor CD and PM Marcus. 2015. *Molecular Modeling of Corrosion Processes: Scientific Development and Engineering Applications*. First Edition. John Wiley & Sons, Inc.

MASTERING HIERARCHICAL STRUCTURES TO TAILOR WASTE FORMS

Abstract

Successful completion of the EM cleanup process includes immobilization of radioactive and chemically dangerous materials in a manner that reduces risk and is stable over a lifespan of many hundreds and even thousands of years. To meet this requirement, a tailored waste form is needed that addresses the properties of the waste material and the specific environment. This waste form should be designed with a structure and chemistry that prevents release of specific atoms as the form interacts with the environment. Thus, elucidating a set of scientific principles that guide the design and construction of waste forms from nano- and mesoscale building blocks, termed hierarchical structures, will bring great benefit in the ability to rapidly create the most functional, durable, and affordable waste forms. These hierarchical architectures represent a construct that will span multidimensional structures across the necessary length and timescales. The ability to create, control, and exploit these architectures is central to the basic science and technology of performance-designed waste forms.

Scientific Challenges

EM wastes require the immobilization of more than 60 elements in varying concentrations, with radionuclides exhibiting varying chemical and physical properties. Further, many of these species are multivalent, changing within the waste forms under varying reduction-oxidation conditions. These resulting waste forms represent an enormously complex chemical system that requires an integrated theoretical and experimental approach spanning multiple scales to reveal fundamental properties that ultimately affect durability and performance. To date, attempts to definitively and accurately determine relationships among composition, structure, and property have been met with limited success.

Incorporation of waste constituents relies heavily on hierarchical structures in the waste form. The number of sites for accommodation of species is immense, as are the possible pathways for transport through the waste form networks. The structures range from atomistic scales, such as the basic unit cell of the host atom and substitutional and defect sites, through mesoscale, including structures with second phases and networks of grain or interphase boundaries. This simple description of hierarchical structures is complicated by the rich chemical environment, which leads to the possibility of chemical segregation and the time-dependent precipitation of new phases, some of which will remain amorphous in structure but others will be crystalline. Thus, the resulting waste form material can be a highly complex, multicomponent composite with widely varying chemistry from one region to the next that then evolves over time. The ideal waste form would tailor structures to optimally contain critical constituent atoms and maintain stability over time in the face of complicated changes due to temperature, pressure, environment, and radiation.

Tailored control of waste form properties requires a fundamental understanding of the dependence of complex materials properties, typically glasses and ceramics, on composition and structure. The ability to design and control these novel materials across the wide spectrum of functionalities and environments is only now emerging and will enable the following:

- New predictive models of structure and property relationships of multicomponent systems
- Mastery of the synthesis and assembly of the hierarchical structures to assure long-term durability
- Scientific basis to facilitate revolutionary approaches for cost-effective waste form preparation and disposition.

Understanding and controlling the structure at the atomistic scale and, eventually, the meso- and continuum scales, are critical first steps in tailoring hierarchical architectures to dramatically improve both waste form production and the resulting performance. The idea is presented in Figure 19 with an example taken from the automotive industry. As an EM-related example, adequately representing the short-range and medium-range order of waste glasses, and the heterogeneous, non-stoichiometric nature of ceramic waste forms (including cementitious, geopolymer, and hydroceramic materials), must be achieved to optimize control at the system level. Representing complex structures and compositions will support obtaining the foundational knowledge to predict and control key phenomena and behaviors with the ultimate goal of optimal waste form performance.

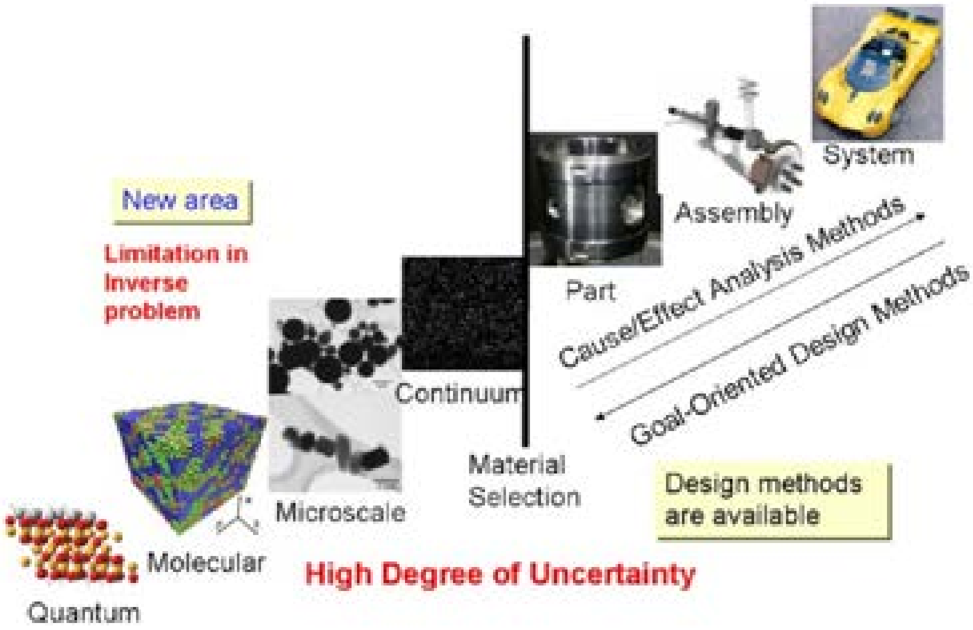


Figure 19. Hierarchy from atomic to continuum in design. This example is from the automotive industry. Traditional approaches focus on system optimization with limited knowledge of the lower scale behavior. Developing scientific principles for waste immobilization that achieve control at the quantum to continuum level will provide greater control of waste stability. Image courtesy of GB Olson (McDowell and Olson 2008).

Research Directions

In this PRD, the following research areas are identified to understand the scientific principles that would allow an optimized hierarchical design of waste forms for specific EM waste immobilization:

- Design and discovery of new material architectures with desired behaviors
- Elucidation of the atomic scale, microscale, and macroscale in complex waste form systems
- Extension of thermochemical, atomistic, and structural modeling to further understanding of physicochemical properties.

These research areas will require a combination of modeling, simulation, and novel experimentation/analyses to understand the composition, structure, and property relationships that allow for the design of hierarchical waste forms.

Design and Discovery of New Material Architectures with Desired Behaviors

Advances in synthesis and improved understanding of crystal chemistry for radionuclides could lead to wholly new classes of materials with long-term durability that could be deployed as waste forms. Advanced materials with tailored nanostructures and chemistry, such as nanoscale composites, nanoclusters, and metal-organic frameworks and related structures, have the potential to be patterned specifically to the waste form application

For example, self-assembled mesoporous materials offer considerable potential for combined radionuclide separations and immobilization. The larger pore spaces and enormous surface areas offer the possibility of incorporation of a wide range of chemical species into the pores. These revolutionary materials are in contrast with conventional approaches employing glass and multiphase ceramic waste forms that rely on atomic-scale incorporation of specific radionuclides into specific crystallographic sites within a ceramic. The subsequent collapse of the structure, either by thermal or chemical treatments, encapsulates the radionuclides. For instance, a silver-functionalized silicon dioxide aerogel with roughly four times higher efficiency in iodine separation has been designed to generate a highly durable waste form of silicon dioxide with nanoencapsulated silver iodine.

The development of new waste form materials will also be accelerated with the aid of modern computational capabilities. Recently, simulations have been used to design a unique apatite mineral for immobilizing of radioiodine that is stable in geologic disposal, contains high waste loading, and can be fabricated using existing technologies (Figure 20) (Wang 2015).

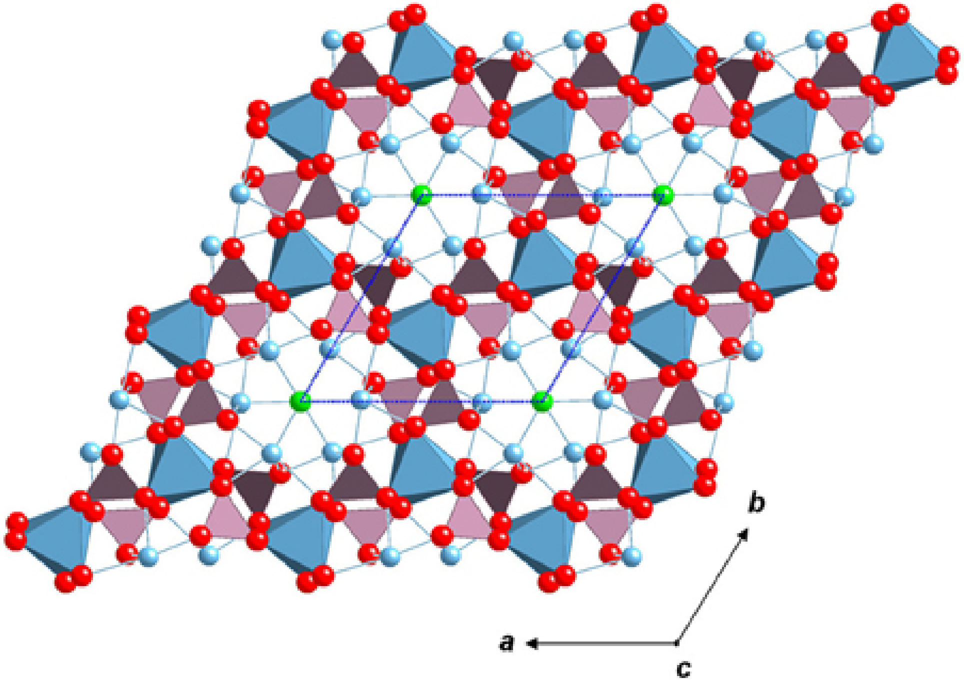


Figure 20. Apatite mineral designed for immobilization of ^{129}I. This is an example of using modern modeling tools to design a molecule that would retain not only a specific isotope of iodine, but daughter atoms that are created as a result of radioactive decay. Image courtesy of Jianwei Wang, Department of Geology and Geophysics, Louisiana State University (Wang 2015).

Elucidation of the Atomic Scale, Microscale, and Macroscale in Complex Waste Form Systems

Understanding and correlating the multiscale performance of waste form materials is required to design the complex systems needed to immobilize waste. A combination of state-of-the-art experimental and computational techniques can offer new perspectives in the structure-property relationships of the atomic-level structure of waste form materials, including order in disordered materials. This research direction focuses on improving the ability to probe and characterize complex systems with increasing fidelity.

Detailed understanding of the atomic structure of glasses is critical for the tunability of their properties. Recent theory originating in France (Calas et al. 2010) proposes that the medium-range structure within complex glasses contributes significantly to waste form performance and dictates how low-solubility ions are incorporated into the glass structure. Although this concept has been acknowledged, little or no research has been conducted on the role of medium-range order in US waste glasses. Short- or medium-range order is difficult both to measure experimentally and to interpret unambiguously; improvements in characterization capabilities to remove this ambiguity are critical to establishing a scientific base of knowledge for developing new waste form materials and, importantly, predicting their performance.

Porosity and interfaces in cements, geopolymers, and hydroceramics are major contributors to radionuclide release. Moreover, these features are present at varying scales (nanometer to millimeter) in these heterogeneous waste forms and little is understood about which features dictate overall performance. Therefore, new characterization approaches are critically needed to elucidate these features in their three-dimensional, time-varying nature.

Direct information on the local and medium-range atomic environment can be obtained through total scattering experiments combined with pair distribution function analysis. A pair distribution function is obtained directly through the Fourier transform of the total scattering structure function. It essentially converts the representation from reciprocal lattice space to real space by including the diffuse scattering contributions that are omitted in traditional diffraction experiments. Pair distribution function analysis can be completed using both X-ray and neutron total scattering experiments. The resolution of the pair distribution function is dominated by the maximum value of Q used in the Fourier transform. The pair distribution function can be refined to extract bond distances, local coordination numbers, and average bond angles; however, the chemical complexity of the waste glasses will greatly challenge experimentation and interpretation of results. Therefore, an improved ability to

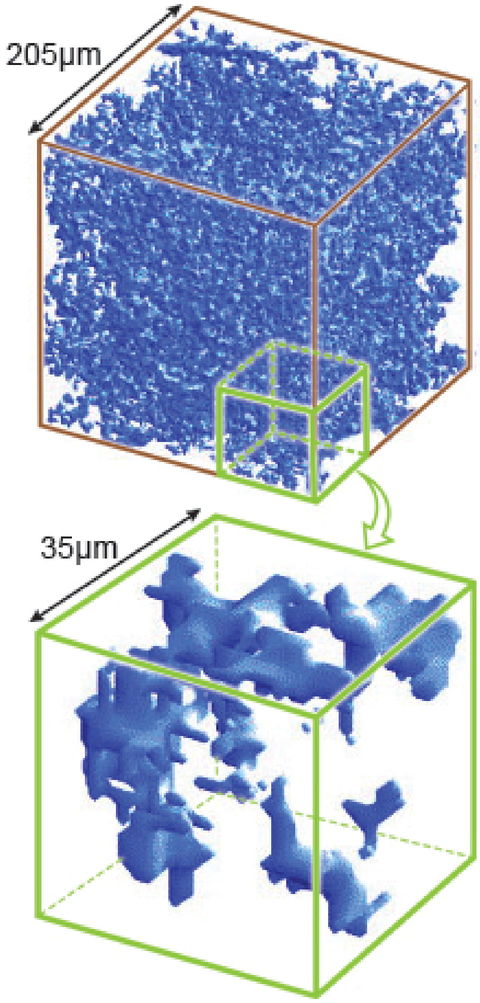


Figure 21. Pore network evolvement in a 3-day-old cement paste (Gallucci et al. 2007). For a material with significant porosity, the ability to control a distribution of interconnected porosity may be critical to ensuring no pathways for release of material can occur through the existing pores. The pores could also be tailored to act as host sites for specific atoms of concern (Calas et al. 2010). Image courtesy of Pacific Northwest National Laboratory.

understand local structures and order, all in a dynamic environment where structures may be changing due to temperature and radiation fields, is a critical scientific gap.

Recent advances in three-dimensional and in situ techniques have made it possible to assess different types and origins of characteristic structure. The networking of glass structure in silicon dioxide has been successfully imaged at atomic resolution using scanning probe microscopy (Lichtenstein et al. 2012). Short-range order was quantitatively evaluated in an Fe-^{18}Al (that is, 82 atom % iron and 18 atom % aluminum) alloy using atom probe tomography data and by calculation of the generalized multicomponent short-range order parameters (Marceau et al. 2015). In situ transmission electron microscopy can play an important role in dynamic studies of waste forms in extreme environments of temperature, corrosion, and irradiation

Atomic packing and short- to medium-range order in metallic glasses have been studied by a combination of X-ray diffraction, extended X-ray absorption fine structure spectroscopy, and reverse Monte Carlo modeling (Sheng et al. 2006). Extended X-ray absorption fine structure is useful to obtain element-specific local coordination information. X-ray absorption near-edge structure spectroscopy can also be used to study the oxidation state in waste forms. X-ray tomography provides spatial distribution of pores, revealing the pore structure in 3D in a nondestructive manner with a spatial resolution of a few microns. For example, in Figure 21, porous structure in cement pastes can be visualized and measured by synchrotron X-ray microtomography (Gallucci et al. 2007). Small pores in waste form materials can also be characterized by X-ray or neutron scattering, as outlined in the *Transformational Research Capabilities* section.

Extension of Thermochemical, Atomistic, and Structural Modeling to Further Understanding of Physicochemical Properties

The ability to build a hierarchical system designed for optimal waste immobilization assumes a detailed understanding of highly interactive, multicomponent systems, far beyond that which exists today. The establishment of advanced atomistic and thermochemical models of glasses and ceramics offer opportunities for new chemistries that could lead to new strategies for bottom-up synthesis of new material architectures with tailored properties. New waste forms that can accommodate higher loading and tolerate higher waste complexity, thermal stresses, and radiation-induced damage can be designed for improved waste retention over geological timeframes. New and novel materials can also be structured to match the waste stream and the intended disposal environment. This research direction focuses on understanding the physicochemical properties including phase separation and crystallization of complex glasses and ceramics.

An understanding of these architectures is required on at least three scales. The first is the atomic or molecular scale, where bonding and local environment prevail (at the molecular scale, short- and medium-range order predominates in glassy materials and long-range order dominates in crystalline waste forms such as ceramics). The second is the microscale, where structural features such as interfaces are important. The final scale is the mesoscale, where macro features such as porosity and surfaces contribute to performance. The fact that many proposed waste forms are glasses or glass matrix composites, where long-range order is frequently missing, complicates the ability to describe a set of hierarchical structures upon which a waste form could be built.

As an example, polymerization representing short- and medium-range order in borosilicate glasses (versus long-range order in crystalline solids) provides flexibility to atomically bind the wide variety of waste constituents within the glass structure. Structural groups form the building blocks for waste glasses and typically consist of tetrahedra of silicon, boron, aluminum, and iron, surrounded by four oxygen ions or boron trigonal units, surrounded by three oxygen ions. These groups join together via bridging oxygen ions. Non-bridging oxygen ions carry a negative charge and facilitate ionic bonding of positively charged cations in the waste forms. The linkages create medium-range order structural groups (depolymerized regions) that can resemble sheet-like, chain-like, and monomer units, often resulting in large cation-rich clusters in the glass. Recent arguments have been made that these cation-rich clusters can lead to channels in the glass that provide preferred pathways for water transport. Insoluble species can also locate in these depolymerized regions precluding incorporation into the glass structure (Figure 22). Therefore, control of the depolymerized regions could enable maximum loading of these insoluble species in the glass. Melt processing parameters such as viscosity are also related to the polymerization/depolymerization characteristics of the glass structure.

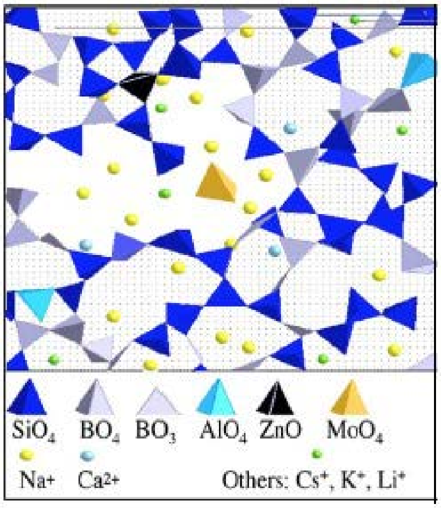


Figure 22. Schematic of a high molybdenum-content high-level waste glass depicting a molybdenum ion located in a large depolymerized region. This is an example of controlling local structure through polymerization as a means of creating specific sites designed to hold a specific atom, in this case molybdenum. Reproduced with permission from Calas et al. (2010).

A key challenge in the study of materials without long-range order is developing detailed atomistic models, which in turn impact subsequent examination of properties. As opposed to crystals, in which atomic coordinates can be reliably obtained from experiments, this is not possible for glasses and other amorphous systems. Approaches in which molecular dynamics are used to anneal a collection of atoms to produce an atomic model of a glass can provide some insight, but there is no guarantee that the resulting structure represents the real material. This is even more challenging as the chemical complexity is increased. Further, understanding transport in these materials is particularly difficult. Transport is governed by a continuum of activation energies, meaning approaches that treat the kinetics as a series of infrequent events, such as accelerated molecular dynamics or kinetic Monte Carlo, often cannot treat these systems. Thus, new approaches must be developed to both accurately determine the structure of glass-like systems and assess kinetic pathways in these complex atomic networks.

Extending thermochemical and atomistic modeling approaches to complex glasses and heterogeneous ceramic waste forms to reveal composition, structure, and property relationships are challenging endeavors. However, success offers the exciting prospect to allow for “network engineering” of hierarchical architectures that could provide game-changing implications to waste form development. For example, glass structures that have a predominance of one type of network over another, eliminating extended depolymerized structures in favor of monomer-type structures, will improve the overall performance.

A fundamental question is how to develop structural models of waste form systems, while considering the complex chemistries possible in these systems, to predict heterogeneities that may occur. Further, the variation in local structure must be connected to the properties of the waste form, such as the ability to immobilize certain chemical species. This requires an integrated modeling approach in which thermochemical modeling is used to understand the high-level phase structure of the waste form as a function of chemistry, focused on the heterogeneous large-scale phase structure of the material. This must, however, be augmented by modeling, both at the atomistic level to determine local structure of the waste form and at the ab initio level to examine how that local structure influences properties.

For example, it is likely that atomistic potentials used to study glasses are not mature enough to accurately capture the complex electronic structure that can occur in these atomic environments and one cannot rely on atomistic simulations alone. Thus, ab initio methods can be used to understand the energetic stability of species within the glass as well as determine the kinetic parameters associated with transport. Further, these methods can be coupled in combined hybrid quantum/molecular mechanics that provide an extended model, capturing the longer range atomic structure but with a central region treated with ab initio methods that provides for chemical accuracy. Finally, mesoscale models that resolve the structure to higher fidelity than possible with thermochemical approaches, but provide a higher level view than pure atomistic methods, are necessary to assess the overall performance of the glass structure or allow for accurate property modeling (for example, viscosity) of the heterogeneous structures. Ultimately, the insight afforded by such studies can provide new pathways to enhancing the properties of glasses, increasing their effectiveness to immobilize species and their overall chemical durability. Such mesoscale models can also be developed to understand how the porosity and interface density in cementitious waste forms govern the ability of the material to sequester radionuclides, providing a path for developing improved materials.

Another important question relates to the surface structure of the waste form as this dictates not only how the glass or ceramic interacts with the environment but how chemical species within the material might experience pathways to escape into the environment. If the local coordination of cations in the bulk dictates the solubility of species, the even more varied coordination on surfaces will determine surface reactivity and the ability of the waste form to contain those species. Thus, there is a need to understand, on the atomistic scale, the structure of these surfaces and how that structure dictates the overall interaction with the environment to better predict—and prevent—radionuclide release. Bulk behavior alone is not sufficient because the surface structure, particularly in porous materials, will ultimately dictate both the interaction with the environment and the distribution of radionuclides within the waste form itself. If there are strong segregation tendencies of species towards surfaces, they will enhance the probability of escape and lead to overall performance degradation.

Technology Impact

This research direction would benefit the EM mission but also have broad effects within DOE and beyond. Specifically, the research will provide new insight into the study of complex materials systems, including the following:

- Pathways for the design and discovery of new material architectures with desired behaviors
- New atomistic and molecular representations of structure and relationships between that structure and material properties at various length and timescales
- Fundamental predictive models developed to design and control properties of multicomponent materials that do not exhibit long-range order.

References

Calas G, L Galoisy, L Cormier, JM Delaye, P Jollivet, and S Peuget. 2010. “Structural Evolution of Nuclear Glasses under Forcing Conditions (Irradiation, Alteration).” *Material Research Society Symposium Proceedings* 1265: 77–88. DOI: 10.1557/PROC-1265-AA03-01.

Gallucci E, K Scrivener, A Groso, M Stampanoni, and G Margaritondo. 2007. “3D Experimental Investigation of the Microstructure of Cement Pastes using Synchrotron X-Ray Microtomography (µCT).” *Cement and Concrete Research* 37(3): 360–368. DOI: 10.1016/j.cemconres.2006.10.012.

Lichtenstein L, M Heyde, and H-J Freund. 2012. “Crystalline-Vitreous Interface in Two-Dimensional Silica.” *Physical Review Letters* 109(10): 106101. DOI: 10.1103/PhysRevLett.109.106101.

Marceau RK, AV Cequerra, AJ Breen, D Raabe, and SP Ringer. 2015. “Quantitative Chemical-Structure Evaluation using Atom Probe Tomography: Short-Range Order Analysis of Fe-Al.” *Ultramicroscopy* 157: 12–20. DOI: 10.1016/j.ultramic.2015.05.001.

McDowell DL and GB Olson. 2008. “Concurrent Design of Hierarchical Materials and Structures.” *Scientific Modeling and Simulation* 15: 207–240. DOI: 10.1007/s10820-008-9100-6.

Sheng HW, WK Luo, FM Alamgir, JM Bai, and E Ma. 2006. “Atomic Packing and Short-to-Medium Range Order in Metallic Glasses.” *Nature* 439: 419–425. DOI: 10.1038/nature04421.

Wang J. 2015. “Incorporation of Iodine into Apatite Structure: A Crystal Chemistry Approach using Artificial Neural Network.” *Frontiers in Earth Science* 3(20). DOI: 10.3389/feart.2015.00020.

PREDICTIVE UNDERSTANDING OF SUBSURFACE SYSTEM BEHAVIOR AND RESPONSE TO PERTURBATIONS

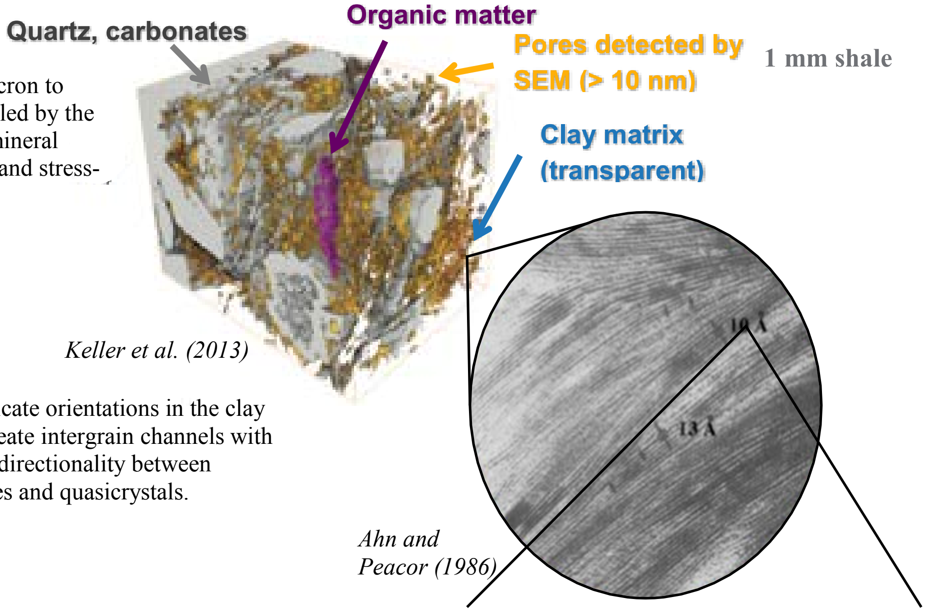
Abstract

Terrestrial system-scale contamination associated with EM wastes includes processes within and across soil, vadose zone, groundwater, and hyporheic and riverine subsystems. Predicting the behavior of subsurface systems is critical to developing methods to control and remediate subsurface contamination. However, this is a particularly challenging task because these subsystems are extremely heterogeneous and difficult to access. These systems involve multiphase flow regimes that commonly encompass complex multicomponent fluid phases that can react with one another and with solid materials. Moreover, many subsurface chemical processes are mediated by groups or communities of microorganisms that work together in complex and poorly understood ways, and that are both responsive to and control subsurface conditions. New approaches are needed to revolutionize the scientific understanding of how biogeochemical processes are incorporated in models of contaminant migration, leading to more accurate process-level predictions. To accomplish the overall goal of system predictability, a better characterization of heterogeneities (physical, chemical, and biologic) and improved understanding of their role in biogeochemical transformations that occur in response to perturbations are needed across a range of scales. To be effectively employed in prediction, these improvements in observation and understanding must be accompanied by computational advances that allow two-way coupling between processes and between highly disparate spatial and temporal scales.

Scientific Challenge

Heterogeneous Spatial Properties and Temporal Perturbations in System Behavior over a Continuum of Spatial Scales

The current understanding of subsurface biological, geochemical, and hydrological process coupling fails to account for the role of heterogeneous spatial properties and temporal perturbations in driving both short- and long-term system behaviors over a continuum of spatial scales. Spatial heterogeneity in subsurface systems greatly influences fluid flow, material transport, and the contained microbial ecosystem and the biogeochemical reactions they mediate (for example, Brusseau 1994). For environmental management applications, challenging problems include the long-term persistence of contaminants in subsurface environments and ineffective delivery of remedial agents to contaminated zones. Both of these problems are influenced by multiscale spatial heterogeneity, in particular the existence of a hierarchically structured network of pore spaces and fractures through which fluids and dissolved or particulate components are transported. It is within this network that microbial communities evolve and chemical reactions and transformations occur. The variable size and structure of solid phase materials comprise a complex geometry that leads to the formation of advection-dominated preferential fluid flow pathways in macropores coupled with diffusion-dominated low-flow domains, often termed matrix regions. These features are common across diverse subsurface environments and typically link across multiple spatial scales. Hierarchies of pore networks are ubiquitous in natural systems (Figure 23).



Pore distributions at the micron to millimeter scale are controlled by the nature and distribution of mineral phases and organic matter, and stress-induced fractures.

Keller et al. (2013)

Phyllosilicate orientations in the clay matrix create intergrain channels with complex directionality between crystallites and quasicrystals.

Ahn and Peacor (1986)

Hydrated interlamellar space at the scale of 1-2 nm exists within individual phyllosilicate crystallites where ion exchange and contaminant reactions occur.

Figure 23. Pores and fractures in subsurface materials exist across scales ranging from angstroms to centimeters. Some of these pores are interconnected, creating a hierarchical network spanning many orders of magnitude in spatial scale. Shales, for example, are dominated by pores in micron and nanometer ranges often associated with phyllosilicates in the clay matrix. Characterizing these pore structures and associated macropore advective domains and integrating their controlling effects into improved reactive transport models is a major research challenge. Image permissions: Top: Reprinted from Keller et al. (2013). Copyright 2013, with permission from Elsevier. Middle: Reprinted from Ahn and Peacor (1986). Reproduced with kind permission of The Clay Minerals Society, publisher of *Clays and Clay Minerals*.

Hierarchically structured pore networks, combined with heterogeneous properties of the solid materials (that is, minerals, coatings, and organic matter of different grain size and physical association) lead to strong local gradients in aqueous fluid composition and microenvironments. These porous media domains are where microbial functions and biogeochemical conditions can differ greatly from bulk averages. Most remedial technologies depend heavily on advective transport for time and cost effectiveness. For example, pump-and-treat methods rely on advective removal of contaminants, and effective delivery of in situ treatment reagents is primarily via advection. Fine-grained materials and small pores have relatively high surface areas (per unit volume) that facilitate surface and bulk-phase reactions with contaminants (such as sorption or precipitation) and reduce contaminant mobility. Therefore, contaminants that enter small intergranular pores and fine-grained porous materials such as clays become resistant to remedial actions through a combination of reduced accessibility to chemical reagents and slow diffusive transport. Contaminants that are sequestered in these low-permeability domains tend to persist in the environment over long timescales and are a major challenge for remediation.

Overlaid on this multiscale heterogeneous spatial structure are temporal perturbations (transient effects) that may drive important changes in the system. Temporal perturbations can be natural (such as floods, droughts, and annual climatic variations) or anthropogenic (such as accidental release of waste into a system or remedial actions), and in many cases, these perturbations serve as the dominant control on the behavior of subsurface contaminants. These can impact a wide range of timescales; for example, mixing groundwater and surface water within riverine hyporheic corridors is driven by river-stage fluctuations over hours, months, and years.

Groundwater-river water exchange driven by river-stage fluctuations, in particular, may cause mixing of waters of diverse composition that can stimulate biogeochemical reactions that are both temporally variable (hot moments) and spatially variable (hot spots). An example of this is shown in Figure 24, where the mixing of Columbia River water (containing relatively high dissolved organic carbon and low dissolved nitrogen) with groundwater (containing low dissolved organic carbon and high nitrate) relieves nutrient limitations and creates localized zones (red hot spots) of enhanced carbon respiration. These hot spots may be further categorized as hot moments because the river water intrusion that creates them is limited to 3 to 4 months annually when snowmelt occurs in the upper Columbia River watershed. Additionally, the timing, magnitude, and duration of their formation is climate dependent, being influenced by winter mountain snowfall, spring temperatures, and other related variables. Such hot spots and hot moments can control the speciation and fluxes of redox-active contaminants (such as technetium, uranium, chromium, and arsenic) from groundwater to surface water, and play a significant role in EM activities. Furthermore, the changes in chemistry and redox state may drive a host of different types of biogeochemical reactions.

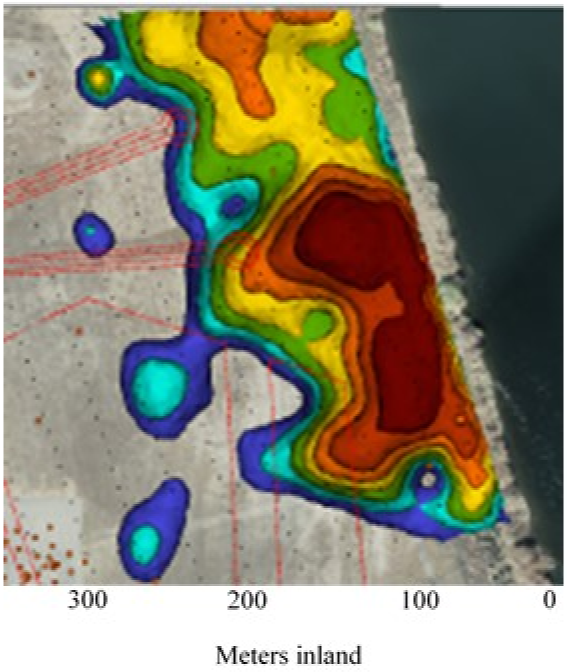


Figure 24. Geophysical measurements sensitive to groundwater salinity and well-water measurements of dissolved organic carbon revealed localized regions of enhanced microbial respiration (red) exist up to 200 m inland of the Columbia River shoreline during the spring high river stage. The hot spots and moments result from the superposition of groundwater-based nitrogen and river-based carbon, as further influenced by subsurface physical heterogeneities that control subsurface water flow pathways and fluxes. Image courtesy of John Zachara, Pacific Northwest National Laboratory.

Predictions of system response to natural and anthropogenic perturbations are needed to guide effective and appropriate remedial actions, monitoring, control, and attenuation, and to properly assess contamination-associated risks. Generally, such predictions are needed at relatively large scales, both spatially and temporally. Robust and accurate prediction (including accurate estimation of uncertainties) is currently limited by the following:

- Lack of understanding of small-scale processes, how they are coupled, and their large-scale manifestation
- Lack of understanding of the relationship between timescales of transient perturbations and system responses

- Inability to characterize the subsurface environment with sufficient spatial and temporal resolution and coverage
- Insufficient computational resources to simulate processes with high fidelity over the relevant space and time domain.

As a result, most application models employ coarse spatial and temporal resolutions, empirical process representations, and fitted parameters—and consequently lack predictive capability.

Research Directions

Remediation of contaminated subsurface systems requires a thorough understanding of relevant biogeochemical processes. Predictive capabilities for heterogeneous systems that span disparate temporal and spatial scales are required to anticipate system response after perturbation. In addition, advancing subsurface characterization by coupling computational capabilities with improved knowledge of hydrogeochemical and biogeochemical transformations will revolutionize contaminant migration models.

Quantify Timescales of Transient-Forcing Events Relative to Response Kinetics

Contaminant transport typically operates over decades, or potentially centuries, being controlled by water migration velocities in the vadose zone and groundwater. Pulsed perturbations that impact transport can occur over much shorter periods (hours to days) and may include precipitation events causing subsurface recharge, groundwater-surface water exchange driven by river-stage changes, and hydrologic manipulation for remediation. Whether these forcings produce nonlinear or emergent long-term effects on transport depends critically on the coupling of hydrologic, geochemical, and microbiologic processes within both advection- and diffusion-dominated domains, the gradients that develop at their interfaces, and the fluxes between them. If responses have long time constants, the system may be unresponsive; if short, they may effectively reach equilibrium with the forcing. However, at intermediate response times, disproportionately large and unpredictable behaviors may result at the system scale. Importantly, response times for abiotic and biotic processes may differ within a given system, causing added complexity and decidedly nonlinear behaviors.

Hydrogeochemical and subsurface microbiological research has recently advanced to the state that highly challenging issues associated with transient conditions and the impacts of perturbation on heterogeneous systems are now tractable. New research is needed to understand the response timescales of biogeochemical and geochemical kinetic processes to dynamic hydrologic events at various time and spatial scales. Experiments are needed to constrain boundary conditions and quantify key relationships and variable dependencies in systems amenable to full physical, chemical, and microbiologic characterization and controlled hydrologic manipulation under both water-saturated and unsaturated conditions. Key to this is considering homogeneous, heterogeneous, and intact subsurface materials exhibiting multiporosity regimes of differing characters. Additional keys lie in the applications of new imaging methods for pore network analysis and molecular methods for functional analysis of microorganisms and their changes. Understanding the dynamics of the biogeochemistry of extreme subsurface environments involving radiation, high pH, and high ionic strength is an important research area. Tightly coupled laboratory and field research is essential to investigate perturbation effects and response times of both pristine and contaminated environments characterized by complex and heterogeneous subsurface structures, physicochemical properties, and microbial communities, and where hydrological events may be extreme, variable, and subject to annual changes.

Advances in genomic sequencing technology and bioinformatics now allow the characterization of subsurface microbial metabolic potential. There is a substantial need to integrate this genomic information into models that account for the dynamic behavior of microbial communities in response to changing environmental conditions. Substantial experimental research advances are also needed to measure the properties of microbial communities in situ to understand their effect on contaminant fate and transport, such as their role in redox transformations of metal ions.

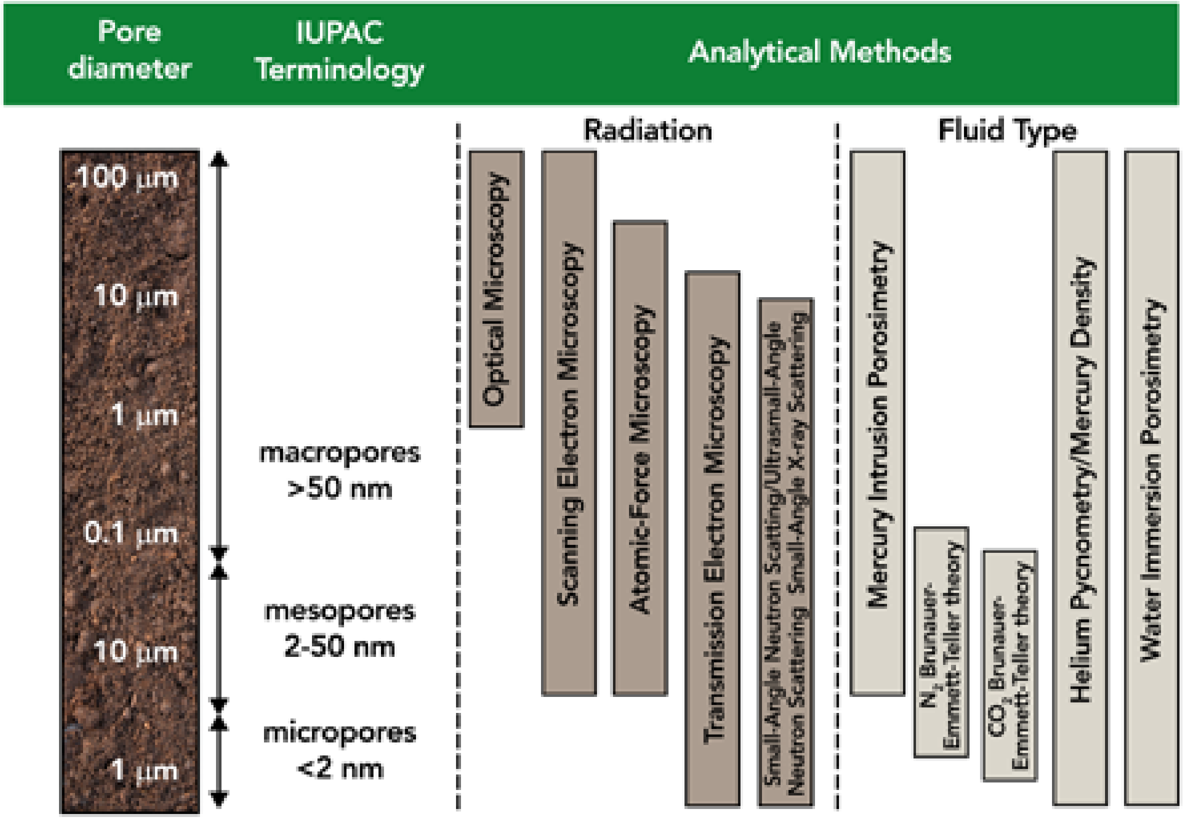
New computational approaches must be developed to examine couplings between and across scales to build a predictive capability of emergent behaviors resulting from nonlinear interactions and responses to perturbations of different types and timescales. A key issue is to determine the reliability of the models and the nature of the time-series data necessary to capture multiprocess responses for dynamic events. How reliable are the models and how much data are needed to robustly establish the impacts of perturbations and identify the causes of response? Well-instrumented experimental facilities, both in the field and in the laboratory, paired with new in situ measurement and computational approaches, are required to test and validate understanding and coupled process models (see the *Transformative Research Capabilities* section).

Elucidate Process Interactions Occurring within Hierarchical Connected Pore Structure

The inherent difficulty in predicting transport through geological materials is that they are highly variable at scales ranging from meters to nanometers. Due to the extreme multiscale nature of reactive transport (phenomena at the nanometer scale influencing transport at the kilometer scale), many processes are necessarily approximated in simulations by effective parameters. The accuracy and robustness of these approximations are questionable. This dictates the need to identify, improve, and/or develop the methodologic “tool kit” to probe the volume under investigation for a range of physical, chemical, and biogeochemical properties (such as density, bulk modulus, porosity, viscosity, permeability, saturation, concentration, biomass, and reaction products). Part of the new challenge is to identify methodologies to represent these properties at all scales to predict system performance after perturbation.

Predictions of plume and contaminant behavior require coupling characterization and process understanding at finer scales with those determined from observations at borehole and greater scales. A critical aspect of this scale connection is determining the intricacies of fluid flow pathways responsible for water movement and solute transport. An essential research need is defining and quantifying a hierarchy of pore types that range from inter- and intraparticle mineral-matrix pores, to organic matter pores, to fracture pores that can host complex fluids and volatiles. Studies are needed to quantify these, not just in terms of shape and size, but how they contribute to the overall fabric of the rock, its ability to host microbial communities and transmit fluids, and the physical properties of the rock itself. The nature of porosity in complex heterogeneous matrices can be interrogated within core samples using state-of-the-art techniques available at DOE user facilities, such as electron microscopy and X-ray and neutron scattering (Figure 25), coupled with more conventional approaches, such as petrophysics, mercury porosimetry, and nuclear magnetic resonance spectroscopy.

The outer boundaries of low-permeability zones can function as interfaces between relatively fast-moving water (in macropores) that is in chemical disequilibrium and slow-moving waters in matrix domains that are in equilibrium with their mineral surroundings. The interchange of dissolved components between these different water types is primarily controlled by diffusion. Chemical transformations and microbial communities tend to be focused at these boundaries, but the nature and prevalence of these presumptive interfacial zones are poorly known. Additionally, geochemical controls exerted by solid phase components (surface reaction and/or precipitation or dissolution) may be spatially correlated with the heterogeneities owing to control by reactive surface area, porosity, mineral identity, and grain coatings. Research to quantify the nature and distribution of these disparate multiscale phenomena, combined with new multiscale simulation methods, would constitute a critical advance in the ability to predict the effect of the heterogeneities on contaminant transport.



Note: IUPAC = International Union of Pure and Applied Chemistry

Figure 25. Characterization methods used to determine porosity and pore size distribution. Image courtesy of Lawrence M. Anovitz (modified from Anovitz and Cole 2015).

Information on larger scale advective-diffusive domain interactions can be gained through geophysical interrogation, tracer tests, and geologically informed inference based, in part, on core assessment. Improvement in these methods is critically needed to advance basic understanding of the subsurface environment and the reliability of transport predictions from often incomplete data sets. To be useful, such experimental methods must resolve heterogeneities at a scale much smaller than that of the contaminant dispersal (<1 m) and must directly relate to parameters controlling contaminant transport, such as permeability, porosity, mineralogy, surface geochemistry, and microbial biomass. Characterization of the orientation and interconnectivity of high-permeability pathways, and their positioning relative to less permeable matrix elements, is vital for EM applications given the importance of less permeable zones to long-term contaminant sequestration and persistence.

Geophysical imaging may support new advances in understanding hydrological and biogeochemical processes occurring in the subsurface. Traditional geophysical characterization methods employ surface-based electrical currents and seismic energy. These methods provide indirect information about subsurface geophysical property variability and require other information to estimate desired hydrogeologic transport parameters. Over the past decade, subsurface characterization has been improved through the high resolution offered by cross-borehole tomography (Figure 26), newer methods such as spectral-induced polarization and geophysical nuclear magnetic resonance spectroscopy, and interpretational improvements resulting from petrophysical studies and joint inversion of geophysical, hydrogeological, and geochemical data sets (for example, Binley et al. 2015; Rubin and Hubbard 2005).

Computational Methods for Adaptive Cross-Scale Coupling of Models to Describe the Impacts of Transient Events on Long-Term Behavior

Subsurface system behavior is extremely complex, involving multiphase flow regimes, chemical processes that are mediated by microbial communities, and interactions among fluids, dissolved constituents, and microbes within the subsurface minerals. These processes occur within and across many system compartments, including soils, vadose zone, groundwater, and river systems, and play out over a wide range of temporal and spatial scales. Developing approaches that can predict the influence of small-scale behavior on larger scale plume flow and transport behavior is a significant challenge that must be tackled to advance EM's mission.

Developing approaches to predict the response of microbial communities to transient perturbations (including remediation treatments) and the associated influence on plume transport is especially important. As pointed out previously, advances in genomic sequencing technology and bioinformatics are now making it feasible to characterize microbial metabolic potential in the subsurface across temporal and spatial scales. Indeed, recent subsurface microbial diversity and metabolic potential discoveries have changed the comprehension of bacterial and archaeal branches. These discoveries have also revealed that genomic information obtained from diverse subsurface communities can provide critical information about biogeochemical processes that impact the quality of groundwater and surface waters (see Brown et al. 2015; Castelle et al. 2015; Hug et al. 2015a and 2015b; Luef et al. 2015; Sharon et al. 2015). Developing approaches to tractably and accurately incorporate genomic and other types of information into plume-scale models, as needed to predict the response of microbial community composition and function to perturbations and the resulting impact on plume mobility, is a critical research challenge.

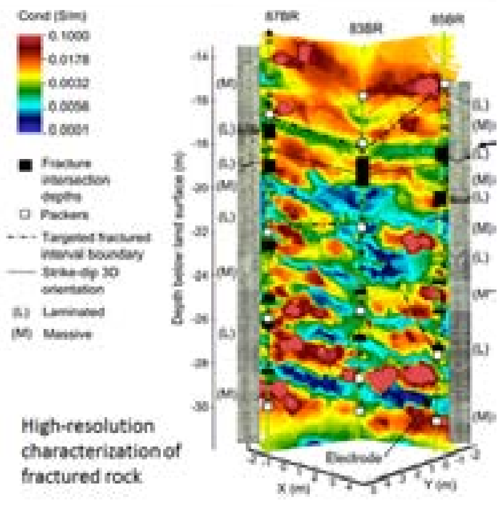


Figure 26. Three-dimensional cross-hole electrical resistance tomogram of fractured mudstone. The image reveals a subsurface structure of alternating conductive and resistive layers similar to geologic layering observed in smaller dimension cores retrieved during observation well placement. Working at a smaller scale, electrical resistance tomogram captured extended geologic features and hydrogeologic heterogeneity controlling flow and transport not evident from core analyses. Image courtesy of Judith Robinson from Robinson et al. (2015).

It is increasingly recognized that the most challenging subsurface problems are not amenable to traditional upscaling methods but require the two-way (up- and downscale) coupling of models with fundamentally different mathematical representations of physics, chemistry, and biology (Scheibe et al. 2015). High-fidelity models, such as genome-resolved models, pore-scale simulations of flow and reactive transport in porous media, have intensive computational requirements. Thus, it is necessary to apply these methods judiciously. This is done by adaptively identifying conditions, corresponding to model subdomains in space and/or time, under which high-fidelity simulations are required—or conversely less complex, reduced-order models can be used. In hierarchically structured subsurface systems, traditional continuum-based reactive transport models may be coupled to pore-scale and even molecular-scale simulations to reduce empiricism and increase model predictive capability. In the context of predicting long-term impacts of system perturbations, it is necessary to consider multiscale and multiresolution methods not only in a spatial sense, but also over variable temporal scales. Thus, advances in computational approaches to couple scales using new concepts from applied mathematics need to be developed, as outlined in the *Transformative Research Capabilities* section.

There is also a need for new hierarchical approaches to quantify model uncertainty. Each scale-specific model has its associated uncertainties, both in terms of model form and parameterization. There is currently little understanding of how uncertainties at one scale impact uncertainties at larger (or smaller) scales (both in space and time). Approaches for quantifying the translation of uncertainty across scales are needed to supplement single-scale uncertainty quantification methods.

Advanced simulators need to appropriately model microbial interactions with mineralogy as well as flow, within the context of the structured subsurface environment and in the presence of transient perturbations. For example, how do the rates of redox reaction change with community diversity and spatial position relative to sources of perturbation? How can genomic data be incorporated into the simulation of reactive flows? Do microbial communities need to be treated beyond a simple lumped reaction approach? How do changes in a community affect reactivity under variable flows with different metabolites? How does microbial growth couple with flow through biofilm development? How do all of these impact the fate of contaminants? These questions represent the new frontier in subsurface transport prediction and urgently need to be answered.

Technology Impacts

The research in this PRD will result in marked improvements in predicting the behaviors of complex subsurface environments containing physical heterogeneities and dynamic, biogeochemically active microbial communities. By focusing on multiscale aspects of subsurface reaction and transport, important scientific insights and significantly improved models will be developed that realistically take into account (1) operative fundamental biologic, chemical, and hydrologic mechanisms and processes; and (2) meaningful pore and geologic structures that control contaminant behaviors and the function of engineered remedial actions. The coupling of this fundamental knowledge with new concepts to model the effects of microbial community function and physical and/or geologic heterogeneities will provide the essential capability to describe and predict the emergent behaviors of subsurface systems and plumes that have not previously been possible.

EM sites were perturbed through waste management or inadvertent materials releases. These initial perturbations continue to be influenced by climatic events and anthropogenic management activities (such as remediation) that create transient conditions of highly varied hydrologic impact and longevity. Understanding the nature and trajectory of response of subsurface environments and their contained microbial ecosystem to perturbations are vital to developing sustainable remediation systems for persistent subsurface contaminants that are the norm for EM sites. Important impacts to EM are anticipated in the following areas:

- Provide fundamental scientific insights to design suitable and cost- and time-effective remediation, control, and attenuation strategies for persistent contaminants of varied physicochemical behaviors
- Establish metrics for more effective site monitoring and characterization that consider impacts of transient events on system behavior and contaminant partitioning between aqueous and solid phases

- Elucidate the impacts of perturbation and transient events on long-term plume evolution and contaminant migration
- Improve conceptual models of contaminated sites to represent emergent effects of fundamental microscale mechanisms at the system scale
- Develop multiscale, process-rich models for reactive transport predictions at the system scale that robustly consider the impacts of dynamic microbial community function and spatially variable pore and geologic attributes.

While targeted at EM mission needs, this research will provide important new knowledge about and predictive models of subsurface systems relevant to multiple DOE missions including enhanced gas extraction, carbon sequestration, and radioactive waste disposal. The research focuses on long-standing unknowns regarding the subsurface environment, such as process response times to perturbations, the functioning of discontinuous hierarchical pore or fracture systems, and causes of and numerical approaches to describe kinetic behaviors of different phenomenology and timescales. In addition, new insights and models will be developed that properly account for the profound influences of subsurface microbiology on a wide variety of subsurface properties and functions. Collectively, insights will be developed to allow control and manipulation of subsurface systems for the benefit of humankind.

References

Ahn JH and DR Peacor. 1986. “Transmission and Analytical Electron Microscopy of the Smectitie to Illite Transition.” *Clays and Clay Minerals* 34(2): 165–179. DOI: 10.1346/CCMN.1986.0340207.

Anovitz LM and DR Cole. 2015. “Characterization and Analysis of Porosity and Pore Structures.” In CI Steefel, S Emmanuel (eds.) *Pore-Scale Geochemical Processes Reviews in Mineralogy & Geochemistry*, volume 80, pp. 61–164.

Binley A, SS Hubbard, JA Huisman, A Revil, DA Robinson, K Singha, and LD Slater. 2015. “The Emergence of Hydrogeophysics for Improved Understanding of Subsurface Processes over Multiple Scales.” *Water Resources Research* 51(6): 3837–3866. DOI: 10.1002/2015WR017016.

Brown CT, LA Hug, BC Thomas, I Sharon, CJ Castelle, A Singh, MJ Wilkins, KC Wrighton, KH Williams, and JF Banfield. 2015. “Unusual Biology Across a Group Comprising 1 >15% of Domain Bacteria.” *Nature* 523: 208–211. DOI: 10.1038/nature14486.

Brusseau ML. 1994. “Transport of Reactive Contaminants in Heterogeneous Porous Media.” *Reviews of Geophysics* 32: 285–313. DOI: 10.1029/94RG00624.

Castelle CJ, KC Wrighton, BC Thomas, LA Hug, CT Brown, MJ Wilkins, KR Frischkorn, SG Tringe, A Singh, LM Markillie, RC Taylor, KH Williams, and JF Banfield. 2015. “Genomic Expansion of Domain Archaea Highlights Roles for Organisms from New Phyla in Anaerobic Carbon Cycling.” *Current Biology* 25(6): 690–701. DOI: 10.1016/j.cub.2015.01.014.

Hug LA, BC Thomas, CT Brown, KR Frischkorn, KH Williams, SG Tringe, and JF Banfield. 2015a. “Aquifer Environment Selects for Microbial Species Cohorts in Sediment and Groundwater.” *The ISME Journal* 9(8): 1–11. DOI: 10.1038/ismej.2015.2.

Hug LA, BC Thomas, I Sharon, CT Brown, R Sharma, RL Hettich, MJ Wilkins, KH Williams, A Singh, and JF Banfield. 2015b. “Critical Biogeochemical Functions in the Subsurface are Associated with

Bacteria from New Phyla and Little Studied Lineages." *Environmental Microbiology* 18(1): 159–173. DOI: 10.1111/1462-2920.12930.

Keller LM, P Schuetz, R Erni, MD Rossell, F Lucas, P Gasser, and L Holzer. 2013. "Characterization of Multiscale Microstructural Features in Opalinus Clay." *Microporous and Mesoporous Materials* 170: 83–94. DOI: 10.1016/j.micromeso.2012.11.029.

Luef B, KR Frischkorn, KC Wrighton, HN Holman, G Birarda, BC Thomas, A Singh, KH Williams, CE Siegerist, SG Tringe, KH Downing, LR Comolli, and JF Banfield. 2015. "Diverse Uncultivated Ultrasmall Bacterial Cells in Groundwater." *Nature Communications* 6: 6372. DOI: 10.1038/ncomms7372.

Robinson J, L Slater, T Johnson, A Shapiro, C Tiedeman, D Ntarlagiannis, C Johnson, F Day-Lewis, P Lacombe, T Imbrigiotta, and J Lane. 2015. "Imaging Pathways in Fractured Rock Using Three-Dimensional Electrical Resistivity Tomography." *Groundwater*. DOI: 10.1111/gwat.12356.

Rubin Y and SS Hubbard. 2005. "Hydrogeophysics." *Water Science and Technology Library,* volume 50. Springer, Dordrecht, the Netherlands.

Scheibe TD, EM Murphy, X Chen, AK Rice, KC Carroll, BJ Palmer, AM Tartakovsky, I Battiato, and BD Wood. 2015. "An Analysis Platform for Multiscale Hydrogeologic Modeling with Emphasis on Hybrid Multiscale Methods." *Groundwater* 53(1): 38–56. DOI: 10.1111/gwat.12179.

Sharon I, M Kertesz, LA Hug, D Pushkarev, TA Blauwkamp, CJ Castelle, M Amirebrahimi, BC Thomas, D Burstein, SG Tringe, KH Williams, and JF Banfield. 2015. "Accurate, Multi-kb Reads Resolve Complex Populations and Detect Rare Microorganisms." *Genome Research* 25(4): 534–543. DOI: 10.1101/gr.183012.114.

TRANSFORMATIVE RESEARCH CAPABILITIES

Introduction

During the course of the workshop, the members of the three technical panels identified six PRDs. Two crosscutting themes emerged from these PRDs. First, the need to understand the many chemical and physical characteristics of EM wastes that are required to design effective, efficient, and safe technologies for waste processing and long-term storage, as well as environmental remediation. Second, the ability to computationally model and thereby optimize the effectiveness of developed technologies, as well as provide a means of predicting the behavior of wastes during processing and long-term storage.

Understanding the complex, multiscale systems associated with remediating waste sites will require new characterization and monitoring techniques, as well as taking advantage of current techniques that have generally not been applied to EM problems. This includes state-of-the-art resources available at DOE user facilities, such as light and neutron sources, radiological user facilities, and nanoscience research centers as well as other specialized facilities located at DOE's national laboratories. Further, the complexity of these waste systems demands multiple analytical techniques to acquire comprehensive insight into the speciation, structure, and dynamics of the chemical systems. To take full advantage of these multidimensional data sets will require new computational approaches to analyze and assimilate massive amounts of data. These data will provide a basis upon which new computational approaches can be formulated to model and even predict chemical and physical processes, from atomistic to macro- scales and from fractions of a second to thousands of years. This information is critically needed to provide holistic mastery of the chemical and physical processes from which will emerge a new generation of enhanced waste processing approaches, new materials and robust forms for waste storage, and innovative approaches for soil and groundwater remediation. This research will generate both new analytical techniques for characterization and long-term monitoring of disposal sites and the environment, along with powerful new computational tools for predicting environmental impacts. Together, these tools will enable the research outlined in the PRDs to increase the efficiency and effectiveness of processes for remediating EM's waste sites, as well as assuring the long-term safety of disposed wastes and monitoring the environment. These transformative research capabilities are detailed below.

Multidimensional Characterization of Extreme, Dynamic, and Inaccessible Environments

Remediation and long-term monitoring of EM waste sites requires analytical tools and sensors capable of characterizing physical, chemical, and biological processes that occur in highly heterogeneous environments and across a wide range of time and space—from nanometers to kilometers and from femtoseconds to centuries. These environments are exceptionally complex because of both their heterogeneity and dynamic nature: each point must be described by the four dimensions of space and time. Add to this a plethora of additional dimensions describing a myriad of chemical and physical parameters. In total, this represents an immense amount of information to provide the optimum approaches for processing, storing, and monitoring these wastes. Finally, the harsh environments and near inaccessibility of the samples presents yet another dimension of complexity requiring special consideration. Undoubtedly, the characterization of many of the wastes at EM sites is among the most daunting challenges that must be addressed before EM can complete its mission. New approaches are critical to provide chemical and physical insights into these complex systems, including new analytical tools and sensors that can provide insight into these extreme, dynamic, and difficult-to-access environments.

Scientific Challenges for Multidimensional Characterization

Strategies for effective characterization of materials associated with EM waste sites need to address some of the most complex chemistries and extreme environments ever considered. It is not sufficient to know just the simple elemental composition of these wastes. Understanding the full range of chemicals in their various forms and associated chemical and physical processes within the entirety of a waste system—whether in storage tanks, waste forms, or the subsurface environment—is a critical first step before effective, efficient, and safe remediation processes can be devised. Characterization approaches must be developed to define vast arrays of chemical and physical parameters of these highly heterogeneous and dynamic systems for a wide range of waste components, including aqueous solutes, clusters, nanoparticles, sorbates, colloids, and precipitates. Further, as outlined in the panel reports, the many types of interfaces involving these components have an enormous impact on the integrated behavior of waste systems. Retention of radioactive species at the interfaces of tank solutions with particulates, if not fully understood, could reduce the effectiveness of remediation processes. Further, understanding the processes by which particles agglomerate could lead to design of processes that avoid clogging pipes.

Additional complications arise from the often inaccessibility of the waste environments. For example, samples from highly radioactive waste tanks are extremely difficult (and expensive) to retrieve and handle. Typically, these samples must be processed in specialized facilities, such as shielded hot cells that are designed to control high radioactivity, and where the types of characterization tools can be limited. As a result, data providing the full picture of the composition, structure, reactivity, and stratification of solid and liquid contaminants in these tanks are currently limited. Similar issues stymie the comprehensive characterization of samples from subsurface environments. In this case, samples must be acquired from boreholes and, as in the case of waste tanks, are expensive and very difficult to obtain, contributing to a scarcity of data. In both cases, ex situ characterization approaches are needed to provide the full range of chemical and physical information required to characterize these heterogeneous and dynamic systems. These ex situ techniques must be highly sensitive to analyze small quantities of materials. Multimodal analysis, using combinations of characterization tools, can maximize the information garnered from each sample.

In situ characterization approaches could greatly reduce the need to obtain samples from these inaccessible environments. For example, waste forms used to sequester hazardous radionuclides are designed to be stored in inaccessible geologic repositories to prevent their release into the environment. It is critically important to monitor the stability of these materials to assure the integrity of these stabilized wastes over centuries. In addition, in situ techniques could provide unparalleled insight into the heterogeneity and dynamics of chemical and physical processes that occur in waste tanks, waste forms, and the subsurface, and could be used to monitor these processes on a continuous basis. However, currently available in situ techniques are far more limited in the types of information provided compared to ex situ, laboratory-based methods. In addition, extreme environments present an exceptional challenge for in situ characterization. Devices must withstand extremes in radioactivity and harsh chemistry, which cause degradation and failure. Remote characterization approaches are another alternative that could circumvent both sampling and degradation issues. These approaches are particularly relevant to subsurface characterization where information is needed over broad spatial and temporal regimes. However, the data that can be obtained with remote analysis are currently even more limited than that available with in situ techniques.

In summary, the full range of chemical, physical, and biological information needed to support the remediation and monitoring of EM wastes is immense. New characterization and sensing approaches that provide multiple dimensions of information on these highly complex, dynamic, and extreme environments are critical for the efficient, effective, and safe remediation and long-term monitoring of the EM sites. Sampling limitations arising from the inaccessible nature of these waste environments demand the development of innovative approaches for high-sensitivity, multimodal ex situ characterization approaches that minimize the amount of required samples while maximizing obtained information. To complement these laboratory-based techniques, new approaches are also needed for in situ characterization methods and remote sensing to yield important information related to the heterogeneity and dynamic nature of these wastes and provide a means of long-term monitoring.

Transformative Research Capabilities for Multidimensional Characterization

The optimum means of characterizing EM's complex waste systems is to evaluate these systems in their natural, in situ environment. Under these conditions, the full effects of components in the context of entire systems can be assessed. However, the extreme environments of tanks and isolation of both waste forms and the subsurface can make this type of direct analysis very difficult. One alternative to in situ analysis for subsurface environments, including waste forms, is remote monitoring, which can be accomplished with arrays of sensors or by aerial surveillance, for example. However, the types of information obtainable from both in situ and remote analysis are currently limited. In contrast, ex situ experiments using state-of-the-art analytical techniques can yield far more detailed information. The disadvantage of ex situ approaches is that obtained information may be skewed when the sample is isolated from its environment. EM's mission requires all three analytical approaches to obtain the most information on chemical and physical processes to develop wholly new approaches to waste processing and long-term storage as well as environmental remediation and monitoring.

High-Sensitivity, High-Fidelity Ex Situ Characterization

To date, most highly radioactive samples have been characterized in specialized laboratories equipped to handle high activity levels. As a result, characterization has been limited to a small set of techniques dedicated to analysis of radioactive samples. Over the past decade, developments in nanoscience have enabled new characterization techniques with unprecedented sensitivity and information collected. As detection limits improve, it may be possible to analyze very small samples, such as materials adsorbed onto nanoparticles or liquids in nano- or microfluidic channels. Limiting the sample size reduces the quantity of radioactivity, making the samples suitable for study using state-of-the-art techniques. This approach, for example, is used to examine radioactive materials in the DOE Office of Science radiological annex of the Environmental Molecular Sciences Laboratory and DOE Office of Nuclear Energy's user facilities. To evaluate the effects of radiation structural integrity, materials irradiated with neutrons at the High Flux Isotope Reactor can be reduced to a very small size with a focused ion beam. This greatly reduces the activity of these samples, allowing them to be analyzed in conventional laboratories with instrumentation such as aberration-corrected scanning transmission electron microscopy and atom probe tomography to enable assessment of radiation damage. Similar approaches are required for studying waste forms and other highly radioactive materials. For liquid samples, reducing sample volume could provide the same type of improved sample handling capabilities. Further, nano- or microfluidic devices could be developed to serve as part of an integrated platform for characterization. In either case, reducing sample sizes can allow a wider variety of characterization techniques to be used.

Indeed, new analytical techniques, or combinations of techniques, make it possible to quantitatively describe the three-dimensional structural, chemical, and mineralogical characteristics of complex waste samples at length scales ranging from angstroms to centimeters (8 orders of magnitude). For instance, atom probe tomography enables the exact three-dimensional reconstruction of the chemical and morphological properties of tiny samples with true atomic-scale resolution. Similar information can be obtained at the nanometer to micron scales using advanced scanning electron microscopy-based imaging and novel approaches such as combined focused ion beam and time-of-flight secondary ion mass spectrometry instruments (Kasel and Wirtz 2015).

To probe structural, chemical, and mineralogical properties of such materials at the micron to centimeter scales, advanced scattering methodologies are available at DOE user facilities, including X-ray light sources and neutron sources. X-ray and neutron scattering and spectroscopic methods are highly complementary, due to the modes of interaction of the beam with the sample. X-rays are highly sensitive to the atomic numbers of atoms in the target, with sensitivity scaling with atomic number (*z*). This allows, for example, X-rays to provide three-dimensional trace element mapping of intact specimens using X-ray fluorescence microscopy. In contrast, neutrons interact solely with atomic nuclei, which have a far smaller scattering cross-section than the electron clouds surrounding individual elements. This enables neutron beams to penetrate far deeper into dense materials than an equivalent X-ray beam, and also permits analysis of samples within vessels, such as high-pressure vessels that duplicate deep Earth conditions. In addition, neutrons are more sensitive to hydrogen than X-rays.

This complementarity is illustrated in Figure 27. Small-angle X-ray and neutron scattering enabled the detailed characterization of the distributions of particles and interfaces where the incident beam encounters a scattering contrast, such as grain boundaries, chemical zoning, or empty versus fluid-filled pores and fractures, at nanometer- to micron-scale resolution. This can be extended to larger length scales by combining ultrasmall angle scattering and backscattered electron imaging. Two-dimensional radiographic and three-dimensional tomographic imaging using X-ray and neutron beams can extend in situ imaging to even longer scales, up to centimeters.

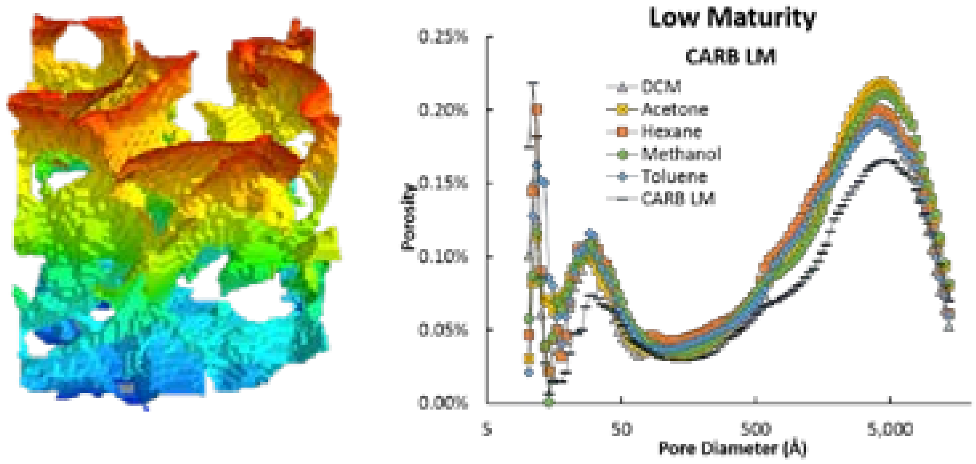


Figure 27. Complementary information on the structure of porous materials. Neutron and X-ray small-angle scattering provide complementary information on the structure of porous materials. In combination with imaging, pore structures can be characterized from the nanometer to the centimeter scale—7 orders of magnitude. Left: X-ray tomographic image of the pore surfaces of a ~2 x 2 x 2 millimeter sample of Domengine Sandston (Anovitz and Franklin, unpublished results). This provides a direct measure of fluid-accessible reactive surface area. Depending on sample size, X-ray tomography can provide resolution down to ~30 nm and very fast imaging rates. Neutron tomography provides lower spatial resolution, but it is able to image larger sample sizes due to the high penetration depth of neutrons. Its sensitivity to hydrogen and deuterium enables real-time imaging of fluid flow. Right: The effect of organic solvent leaching on the pore structure of a sample of the Eagle Ford Shale, a tight oil/gas shale from the gulf coast of Texas (Anovitz et al., unpublished results) obtained from small-angle neutron scattering research at the Spallation Neutron Source at Oak Ridge National Laboratory. Images courtesy of Oak Ridge National Laboratory.

For techniques that rely on DOE's photon- and neutron-based user facilities, the X-ray or neutron energy is extremely important to achieve high values of momentum transfer (high Q) and ideally provide high resolution over the entire Q range. New generation X-ray and neutron sources are coming on line or are being planned that will deliver higher average brightness. These new capabilities will be essential for studying EM materials such as waste forms. A new generation of optics and detectors must be developed that will allow these beams to be focused, which will improve spatial resolution. For example, detectors could be designed to reveal chemical composition and bonding in three dimensions and in real time, making more efficient use of every X-ray and neutron produced by the source.

Recent advances in nanoscience have given rise to techniques that can be applied to samples associated with EM wastes and can inspire a new generation of highly selective and information-rich characterization tools. Optical spectroscopic techniques now make it possible to detect single molecules (Walt 2012). For example, vibrational sum frequency generation microscopy now makes it possible to characterize molecules attached to single nanoparticles and could be applied to understand the interaction of various solutes with particulates formed in waste tanks.

State-of-the-art imaging using electron microscopy, scanning tunneling microscopy, and atomic force microscopy now makes it routine to visualize materials with high sensitivity and high spatial resolution—nanometer and even atomic resolution. Further, in situ imaging methods now make it possible to study materials under realistic conditions. One example is the adaptation of small environmental electron microscopy cells with electron-transparent silicon nitride windows that can hold a small volume of electrolyte, an example of which is shown in Figure 28 (Chee et al. 2015). Cells like these have been used to probe battery systems, for example, but could shed unique insight into atomic-scale corrosion processes, waste forms, and others systems of interest to the EM mission.

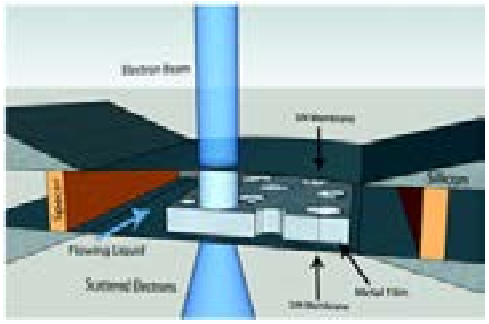


Figure 28. Schematic of in situ liquid transmission electron microscopy cell. Reproduced from Chee et al. (2015) with permission from the Royal Society of Chemistry.

However, many imaging techniques are limited with respect to providing chemical information, and new modalities of imaging are needed to address this gap. For example, photoinduced force microscopy provides spectroscopic information on materials with resolution of less than 10 nm (Jahng et al. 2015). Further, emerging spatially resolved surface sampling and ionization techniques coupled with mass spectrometry are enabling the direct elemental, molecular, and macromolecular chemical characterization of interfaces (Lorenz et al. 2014). These and other "hyphenated techniques" that combine different analytical capabilities provide the opportunity for unprecedented chemical and functional characterization of materials and interfaces with little to no sample preparation.

An additional gap in characterization techniques is encountered when studying systems far from equilibrium. For example, current analytical techniques are limited in their ability to characterize materials under extremes of radiation. In this situation, alpha-decay events result in collective processes over femto- to nanosecond timeframes that drive the local atomic structure far from equilibrium. The energetic helium particles lose their energy predominantly through inelastic interactions with electrons, leading to local states of intense electronic excitation: a confined plasma-like state. Through electron-phonon coupling, the excited electrons transfer their energy to atoms, which are rapidly heated, resulting in nanoscale defect formation during fast quenching processes. There are no characterization tools to monitor the atomic-scale structure during such highly transient events, which limits fully capturing the defect-formation process. These highly localized defects are nonequilibrium regions evolving in materials over long timescales (from seconds to millennia) and interacting with each other during defect accumulation in a radiation environment. While ion accelerator experiments are currently used to study structural evolution of materials under intense irradiation and picosecond cascade damage processes are being indirectly investigated by transmission electron microscopy with in situ ion irradiation at liquid helium temperature, the long-term evolution of nonequilibrium states is inaccessible by current experimental approaches. Computational modeling has the potential to provide insight across this hierarchy of timescales from short-time processes inaccessible to current experimental probes (such as the details of collision cascades) up to the geological timescales over which these materials evolve.

Information-Rich In Situ and Remote Characterization

Online characterization and remote monitoring techniques are often used for industrial process monitoring and other applications where real-time measurement of various physical and chemical parameters is required. These techniques can provide insight into physical parameters, such as temperature, flow, and levels of particulates, and simple chemical measurements, such as monitoring of one or more chemical component. A new generation of sensors and in situ characterization techniques are critically needed to provide more detailed chemical and physical information in support of EM's mission. First, the ability to analyze and monitor EM wastes in real time without having to retrieve samples would be the ideal way to obtain the most accurate assessment of the chemical and physical environment, including insight into dynamic processes. Second, in situ analysis would circumvent difficulties with the heterogeneity of these environments and obtaining representative samples. Finally, in situ and/or remote monitoring of waste tanks and associated processes, waste forms, and the subsurface in real time could assess changing chemical and physical parameters that impact the stability of these environments over time.

New approaches for real-time monitoring must provide as much chemical and physical information as possible. For example, sensors could be designed to monitor multiple chemical components or parameters simultaneously. Importantly, these monitoring devices must withstand the extreme environments associated with EM wastes. While the requirements for in situ characterization and remote monitoring of EM wastes are extremely challenging, development of these new capabilities could revolutionize understanding of these dynamic and heterogeneous systems more completely and provide a means of monitoring wastes and processes in real time.

New approaches are also needed for characterizing environmental systems over large spatial domains. For example, injectable tracers could be used to image subsurface transport by standoff detection techniques or unmanned aerial vehicles equipped with specialized instrumentation. Energy-harvesting microchip sensors could be developed to autonomously sample geochemical and biological properties, or to perturb the local environment and measure the response. For example, advances in high-throughput genome sequencing combined with biogeochemical transport models to integrate this information could achieve comprehensive, functional prediction of the metabolic spectrum of microorganisms. This could profoundly affect the fate and transport of radionuclides in subsurface environments. It may be possible to develop proteome microdevices that quantify and transmit information on enzyme activity for key biogeochemical transformations occurring below the surface. This type of biomonitoring would be especially sensitive to elucidate cryptic, high-flux reactions, where the chemical products of one reaction are masked by a subsequent rapid abiotic or biotic reaction. Ultimately, the rapid and sensitive monitoring of microorganism responses could yield continuous, aquifer-wide data to identify transient perturbations impacting biogeochemical processes, distribution of hydraulic flow paths, and contaminant plume migration.

In summary, achieving EM's mission requires significant advances in all three types of analysis and monitoring—ex situ, in situ, and remote. It is clear that current knowledge of the chemical and physical parameters and processes occurring in tank wastes, waste forms, and the subsurface falls far short of what is needed to support the design of new technologies. Advances in characterization gained as part of this research area will have a huge impact in other DOE applications that require high-sensitivity and high information-content characterization tools. Close coupling with new computational tools is critical for analyzing and simulating data, and can also provide predictive insight into the behavior of these wastes during processing and storage.

Integrated Simulation and Data-Enabled Discovery

The complexity and inaccessibility of the EM waste systems present a daunting challenge for the completion of the EM mission. First, to get a complete picture of the chemical and physical parameters affecting these complex waste systems, many types of experimental measurements are needed, producing a vast quantity of data that must be analyzed and assimilated. Second, the data may be extremely difficult to obtain due to inaccessibility or the broad spatial and temporal scales that need to be bridged. In both cases, a new generation of computational capabilities will be indispensable for complementing characterization and monitoring techniques. Members on each of the workshop panels noted that an integrated approach closely coupling experiment with data science and computational tools could revolutionize the environmental management effort and provide enhanced insight into waste characteristics. In addition, this coupled approach will support many other aspects of EM's mission, including scientific risk/failure analysis, compliance metrics, and long-term health and safety. Achieving such a capability will require new theories and algorithms that fuse, extract, and analyze large, heterogeneous, and incomplete data sets. This will dramatically enhance information content and provide a holistic understanding of the interactions and transformations of contaminants from the molecular to the system scale and from nanoseconds to centuries. At the same time, understanding the evolution of wastes will require advanced modeling, simulation, informatics, and automated learning algorithms that effectively use high-performance computing platforms to bridge these broad spatial and temporal scales.

Scientific Challenges for Integrated Simulation and Data-Enabled Discovery

The challenges to characterize, remediate, and monitor contaminated sites effectively on massive scales require a new generation of computational approaches. Methods must be developed to extract the most relevant information from vast and often incomplete data sets, including techniques that classify and recognize subtle patterns in data that require further analysis. New computational methods and algorithms are needed to bridge information from the molecular to the macroscale. A particular challenge will be development of techniques to study processes far from equilibrium, such as those found in the extreme conditions that exist in EM wastes. Also needed are techniques that can scale in size and complexity to accurately represent, and even predict, a real system. In the context of these two broad scientific domains, two major research areas were identified that cut across all of the panels:

- Data-enabled scientific discovery
- Advanced modeling and simulation with predictive capabilities.

Data-enabled discovery requires major enhancement of the current capabilities to fuse, extract, and analyze data from a broad range of experimental techniques and computational simulations. Data fusion requires disparate individual data sets, potentially of different dimensionality, sampling size, and containing different attributes or variables, be integrated into a consistent, accurate, and useful representation. Modeling and simulation techniques that take advantage of DOE's extensive high-performance computing resources are needed to more accurately describe the underlying chemistry and physics of these complex waste systems and project these processes across broad length and timescales. Currently, at the molecular to nanoscale, some techniques (such as statistical mechanical methods) are naturally parallelized for use on modern high-performance computers. Others (such as electronic structure approaches) require significant development to effectively use internode parallelism, on-node parallelism in terms of threads, and on-core parallelism in terms of vectorization. Thus, this new generation of approaches must efficiently handle the full range of electronic structure, atomistic, coarse-grained, and continuum modeling tasks.

In summary, new computational and data analytic approaches coupled with data validation and verification are needed to extract, analyze, and assimilate information from the relevant data. These developments, when closely coupled, present an enormous opportunity to revolutionize the understanding of the highly complex environments of EM wastes and provide powerful new predictive capabilities. This will allow scientists to identify unknown gaps in knowledge and develop more efficient processes and safe, long-term disposal options.

Transformative Capabilities for Integrated Simulation and Data-Enabled Discovery

The ongoing data explosion, initiated by advances in electronic communications and dissemination of knowledge that began in the late 20th century, continues to be a source of innovation among many disciplines. As a result, mathematical approaches have been developed to analyze complex data sets; however, none are directly relevant to the types of data that describe EM wastes. New analytical data need to be generated to describe tank wastes, waste forms, and subsurface environments for the completion of the EM mission. Generation of vast amounts of new data will necessitate the concomitant development of computational techniques for assimilating and analyzing this data to devise improved chemical processes and materials. Further, the development of next-generation modeling and simulation capabilities, along with the emergence of exascale computing at DOE facilities, represent an unprecedented opportunity for knowledge inference or discovery of complex and largely inaccessible contaminated systems. These capabilities would enable a transition beyond the characterization of isolated “parts” of a contaminated environment to a seamless understanding and prediction of integrated system behavior.

Data-Enabled Scientific Discovery

Data that is currently produced from experiment and modeling represents many dimensions of information—not only the four dimensions of space and time, but the associated chemical and physical parameters at each point. However, the length and timescales and information content of these different experimental measurements and computational simulation data are generally disparate; thus, it remains a scientific challenge to effectively assimilate and gain useful information from the data. Methods for data fusion are needed to circumvent the inherent challenges represented by EM wastes, namely the size, heterogeneity, dynamics, and incompleteness of the data. Such methods can enable predictive models of waste behavior in tank processes, waste forms, and in the subsurface. Further, data analytics approaches applied to fused data sets have extraordinary promise for revealing unknown correlations of behavior and transformation across broad time and length scales as well as the feedback and correlation of seemingly unrelated phenomena and properties. The essential scientific challenge is to enable the development of next-generation computational capabilities that are needed to assimilate and interrogate these data. Coupled with new characterization and monitoring techniques, these new capabilities will enable data-driven predictive science that will allow new technologies and processes for handling, disposing, and monitoring wastes and supporting EM decisions.

A critical first step is to establish highly curated databases that collect, store, index, and disseminate large volumes of unprocessed experimental data as well as distilled, first-principles data from simulations. These databases will require data fusion approaches that assimilate, compare, and combine different types of data on specific samples. Thus, this effort will represent a significant “big-data” problem that derives from enhanced multidimensional data from ex situ experiments, in situ characterization, and remote monitoring. It will also be important to develop mechanisms to link high-accuracy results to these databases and make them available to the community in a timely manner. A perspective article provides additional insight on how theory and experiments may be linked through big-deep data (Sumpter et al. 2015).

While these computational capabilities must necessarily begin with simple systems, approaches must be developed to analyze and simulate (algorithmically and numerically) increasingly more complex systems that represent EM waste environments. These capabilities are critical, for example, to guide the next steps of a laboratory-based basic science experiment or make critical decisions based on field-acquired data. Continued development of analysis algorithms and infrastructure for curating the collected data could eventually involve machine learning techniques. These techniques enable computers to identify specific features in data and algorithms to judge data in terms of quality and information content (unsupervised and supervised learning).

Advanced Modeling and Simulation with Predictive Capabilities

Modeling and simulation could provide a framework that passes both equilibrium and dynamic information across scales, potentially enabling rational design of new waste forms. A predictive understanding of the atomistic- to micro- to macro-structural evolution of waste tanks accounting for radiative environments and a seamless understanding of the interfacial processes in the geosphere that will model plume flow into geologic timescales are also possible. However, significant advances are needed to develop new software and algorithms to fully realize these capabilities. For example, new approaches are needed to accurately address the complexities inherent in EM systems and discriminate between closely competing processes. These new algorithms must also bridge length and timescales necessary to assess materials features, such as domain walls, grain boundaries, and changes in composition, structure, and dynamics. Currently used theory-based calculations lack a reliable accuracy and cannot easily treat the multiple length and timescales required.

For example, the materials associated with EM waste forms are far more complicated than the simple structures typically studied in small periodic unit cells by electronic structure calculations. They are also subjected to extremes of radiation, which causes these materials to be far from equilibrium. Because many of the critical reaction processes involved in materials irradiation occur at very short timescales and continue over very long timescales, characterization tools are limited in providing critical insight. New computational modeling techniques are needed to provide insight across these extremes of scale and complement experimental techniques.

The large length and timescales, as well as finite temperatures, make even density functional theory calculations for investigating materials under relevant conditions prohibitively expensive. Grain boundaries, extended defects, and complex heterogeneities further complicate this issue. Improved model fidelity needs to include uncertainty quantification, especially when embedded in a multiscale model/simulation. However, uncertainty quantification approaches must be developed in close collaboration with both the chemical and materials modeling and simulation communities as well as experimentalists to set appropriate standards. In addition, there is a need to fully glean information contained in experimental data for input into computational methods to predict and understand the materials and chemical processes. This will require integrating data efficiently from different modalities of characterization techniques to provide a more complete perspective on materials structure and function.

In the context of waste forms, prediction of materials properties and performance necessitates an understanding of the interplay among energy transfer and accumulation (radiative environment), materials chemistry, external environment, and evolution of its structural and physical properties over time. Addressing these issues requires an ability to connect molecular-scale details of the involved interactions to the mesoscale behavior of the material. In addition, an understanding of the interplay between the various processes is needed, which is predicated on the ability to provide sufficient accuracy in the models and access the relevant energy, length, and timescales simultaneously. It would be highly beneficial if a large number of structure-property relationships could be derived a priori based on first-principles simulations.

Further, bulk and interface structures often play vital roles in the physical and chemical processes in nearly every system described in this report. New functionality could be discovered through deep analysis and modeling of the multiple interfaces and inherent gradients (structure and dynamics) across these into the bulk. Interfaces exhibit properties associated with the nanoscale in one dimension and the macroscale in others. This leads to unique physico-chemical characteristics and reactivity essential to the success of a device or process. Reactive phenomena, such as redox reactivity, and solvent effects require accurate quantum mechanical treatments that capture the localized nature of these processes while employing realistic boundary conditions. It is necessary to move beyond cluster models from quantum chemistry as representing interfaces and embed models in realistic electrostatic environments. This may include quantum and molecular mechanic approaches and the development of enhanced embedding methods.

In terms of complexity, the multicomponent solutions in environmental management and waste processing can often exhibit emergent behavior. Here, high ionic strength, extreme pH, complex crystallization, precipitation and dissolution, microenvironments, and phase separation may be combined. Advances in theory are required for techniques that provide information about the composition, diffusion, and flow of solutes, gases, precipitation, dissolution of solids, and nucleation events in the complex environments of waste forms, waste tanks, and the subsurface. Force-field development is a long-standing challenge, particularly those transferable to complex solutions. Finally, interdisciplinary methods that leverage information science are needed to elucidate correlating relationships between local and extended structure and dynamics of complex solutions, enabling predictive theories for energy and mass transfer, aggregation/phase phenomena that hinder the rational design of new catalysts, materials, and optimal conditions. Thus, development of new computational capabilities for modeling and simulation is critical to both interpreting data and predicting the behavior of materials and processes over broad temporal and spatial scales.

Summary

The sheer complexity of EM wastes must be fully understood to provide effective, safe, and secure long-term solutions for waste storage and environmental management. Successful characterization approaches must take into account the enormous variations in contaminated materials; ongoing chemical, physical, and even biological processes; and local geochemistry. These variations are enormous and it is not currently possible to generalize data or conclusions between sites or even within a site. Inside a specific system, such as a tank, waste form, or geologic formation, the material and chemical properties differ enormously across temporal and spatial domains. The complexity is further compounded by challenges associated with system inaccessibility, inhomogeneity, and extremely harsh conditions.

Advanced computational tools are required to interpret and assimilate data to assist in the full characterization of EM wastes and sites. Further, the behavior of the wastes during processing and in long-term storage must be understood and modeled. The challenges associated with meeting the needs of the EM mission require a unique blending of information that is large, highly disparate in spatiotemporal scales, heterogeneous, and incomplete to successfully and effectively characterize, monitor, and remediate contaminated sites on a massive scale.

Characterization of chemical, biological, and physical processes, as well as materials science, have advanced significantly in the past decade due to new capabilities available at DOE X-ray and neutron sources, and advances in electron microscopy, scanning probes, chemical imaging, and spectroscopy. In addition, the last decade had enormous advances in the power of computers—now approaching the exascale—and development of codes that take advantage of new computing capabilities. These two major areas of development, when closely coupled, present an enormous opportunity to revolutionize the understanding of the highly complex environments of EM wastes and provide powerful new predictive capabilities for design of disposal processes. The needs in this area are particularly challenging because of the inaccessible nature of the subsurface and storage environments, the heterogeneous nature of waste materials, and the need to estimate behavior for long timescales. The enormous magnitude and scope of the EM mission lends a special urgency to develop next-generation characterization and computational tools to meet this challenge.

The advances outlined in these research directions will provide the scientific foundation to predict the behavior of inaccessible systems that extend to geological scales but are driven by nanoscale processes. These capabilities will allow EM to confront complex systems with enhanced confidence and develop new processing approaches to bridge empirical to highly robust treatments of dynamic systems. Many energy-related applications involve materials and chemical processes operating in extreme environments of irradiation, temperature, pressure, chemical corrosivity, or electric fields (Hemley et al. 2009); thus, understanding extreme environments is critical to advance new energy technologies. The characterization and modeling capabilities that will be developed for nuclear waste applications are directly applicable to a broad range of energy research fields.

References

Chee W, SH Pratt, K Hattar, D Duquette, FM Ross, and R Hull. 2015. "Studying Localized Corrosion using Liquid Cell Transmission Electron Microscopy." *Chemical Communications* 51: 168–171. DOI: 10.1039/C4CC06443G.

Hemley RJ, GW Crabtree, and MV Buchanan. 2009. "Materials in Extreme Environments." *Physics Today* 62(11): 32. DOI: 10.1063/1.3265234.

Jahng J, DA Fishman, S Park, DB Nowak, WA Morrison, H Kumar Wickramasinghe, and EO Potma. 2015. "Linear and Nonlinear Optical Spectroscopy at the Nanoscale with Photoinduced Force Microscopy." *Accounts of Chemical Research* 48(10): 2671–2679.

Kasel B, and T Wirtz. 2015. "Investigation of the Depth-profiling Capabilities of the Storing Matter Technique." *Journal of Mass Spectrometry* 50(10): 1144–1149. DOI: 10.1002/jms.3632.

Lorenz M, OS Ovchinnikova, V Kertesz, and GJ Van Berkel. 2014. "Controlled Resonant Surface Tapping-Mode Scanning Probe Electrospray Ionization Mass Spectrometry Imaging." *Analytical Chemistry* 86: 3146–3152.

Sumpter BG, RK Vasudevan, T Potok, SV Kalinin. 2015. "A Bridge for Accelerating Materials by Design." *NPJ Computational Materials* 1: 15008. DOI: 10.1038/npjcompumats.2015.8.

Walt DR. 2012. "Optical Methods for Single Molecule Detection and Analysis." *Analytical Chemistry* 85(3): 1258–1263. DOI: 10.1021/ac3027178.

SUMMARY

Over the past 25 years, the Office of Environmental Management (EM) has made significant progress in remediating many of the legacy nuclear production and research sites that date back to the earliest days of the atomic era. Completion of EM's mission at the remaining sites represents a far greater challenge, however. This is due to the extreme complexity and hazardous nature of materials present in high-level radioactive waste storage tanks that must be processed and prepared for safe, effective long-term storage. In addition, many of these sites have extensive subsurface contamination that must be addressed. As outlined in a report by a task force of the Secretary of Energy's Advisory Board (SEAB 2014), wholly new technologies are needed to help EM complete its mission more efficiently and safely and in a timely, cost-effective manner. The task force concluded that these advances will not be met by simple, incremental changes in today's technologies; rather fundamental science was needed to provide a foundation upon which vastly improved technologies could be based. This workshop, Basic Research Needs for Environmental Management, was tasked by the Office of Science to identify the most promising fundamental research directions that could address current technology gaps in waste processing, long-term storage, and subsurface contamination and provide the foundations for a new generation of technologies to ensure that EM's mission goals are met.

Many of the technical gaps identified before the workshop (as outlined in Appendix A) were centered on a common theme of the systems under extreme conditions that we are currently unable to master and exploit. For example, the environment inside high-level radioactive waste tanks represents conditions very far from equilibrium that are responsible for driving unexpected chemical and physical processes. In these dynamic systems, myriad metastable, transient components collectively lead to surprising behaviors that are poorly understood. For example, radiation exposure over long periods of time causes a cascade of events that can lead to failure of structural materials and waste forms and subsequent release of hazardous materials into the environment. Our current understanding of these systems is based on much simpler conditions that are at or near equilibrium, for example, they are changing very little over time. Thus, a critical first step in understanding these dynamic systems is elucidating the full range of species and processes that occur. Armed with this knowledge, it may be possible to control these processes and reduce the complexity of the systems, resulting in more efficient and cost-effective remediation schemes for waste handling and processing. This knowledge will also enable the design of new generations of robust materials for waste processing and long-term storage.

Another common theme identified in the technical gaps was the need to understand the highly heterogeneous nature of the wastes and the diverse interfaces involved, including tank waste solutions with suspended particulates, contaminated groundwater with minerals, and corrosive solutions with tank materials. Understanding these various interfaces, across broad spatial scales—from the atomic to system levels—could have an enormous impact on EM's mission. For example, the interaction of radionuclides with subsurface particulates must be understood to develop models that predict the fate and transport of these materials in the environment. Understanding chemical and physical processes that occur at interfaces is critically needed to develop corrosion-resistant structural materials for waste processing and durable waste form materials that can last for centuries. Understanding interfacial processes is also critically important for the development of new separations schemes that could be used to prepare wastes for long-term storage or cleanup of environmental contamination.

A third theme identified from the technical gaps was the lack of robust and resilient materials with properties specifically designed for optimized performance. In the case of processing tank wastes, for example, materials could be designed to remove targeted species selectively from the complex mixtures in preparation for long-term storage. Similarly, waste forms could be designed to improve the storage of hazardous materials and allow them to be stored safely for hundreds and thousands of years.

The six Priority Research Directions identified by the workshop panelists reflect these three themes, which represent some of today's most challenging areas of science. Indeed, the recent report, *Challenges at the Frontier of Matter and Energy: Transformative Opportunities for Discovery Science* (BESAC 2015), specifically calls out characterization and control of matter far from equilibrium and understanding the role of heterogeneity and interfaces as two of the Grand Challenges for the scientific community.

Despite the enormity of the research challenges identified, the panelists were overwhelmingly confident that now is the time to bring the broad capabilities of the Office of Science to bear on these research needs for the EM mission. For example, the panelists noted that over the past decade, significant advances have been made in understanding materials and chemical processes at the nanoscale. These advances have been enabled with investments in basic research in nanoscience, materials science, and biogeochemistry, especially with concomitant advances in high-performance computation and characterization tools. For example, high-performance computing and associated modeling and simulation algorithms are making it possible to model chemical and physical processes over increasingly larger time and length scales, which is of high relevance to EM's needs. These advances are also making it possible to design new materials with specific functionality that could be used to design a new generation of materials for enhanced separation processes. Further, new imaging tools can now study materials under realistic conditions, allowing materials interfaces to be understood.

In addition, considerable progress has been made in mathematics, computational algorithms, and high-performance computing over the past decade. These capabilities will enable the massive quantities of data that will be generated from multidimensional characterization techniques to be analyzed and assimilated, providing insight into the many chemical and physical processes that occur in these complex, dynamic systems.

As the panelists summarized in the *Transformational Research Capabilities* section of this report, new characterization and computational capabilities will be needed to fully address many of EM's existing technical gaps; many capabilities currently exist at US Department of Energy user facilities, including nanoscale materials science research centers, radiological user facilities, X-ray and neutron sources, and high-performance computation centers. However, few of these state-of-the-art capabilities have been applied to the types of systems encountered at EM sites. Thus, there is an exceptional opportunity to take advantage of these and other advances in basic science to address the identified technical gaps required to meet EM's mission needs.

The workshop panelists were also confident that the Office of Science represents the full range of disciplines required to immediately begin to address these EM challenges, including chemistry, materials science, geochemistry, actinide chemistry, biology, environmental science, and computational science, among others. The Office of Science's multidisciplinary approach is critically important to the success of the research directions outlined in this report. The panelists also realized that these areas of basic research would provide an outstanding opportunity to engage the next generation of scientists to conduct research as part of these Priority Research Directions and to provide a pool of qualified people with expertise to carry out environmental restoration at EM sites in the future. In addition, the panelists noted that this research would provide underpinning knowledge that is broadly applicable to other areas of the US Department of Energy's mission, including separations methods for critical materials recovery and isotope production, robust materials for advanced reactor and steam turbine designs, and new capabilities for examining subsurface transport relevant to the water/energy nexus.

There is no doubt that the technical gaps addressed during the workshop represent some of the most challenging areas in science today. However, at the close of the workshop, the panelists were confident that these gaps could indeed be met with a sustained commitment to basic research. This research would focus on understanding the multitude of chemical and physical processes that occur in these complex systems that are far from equilibrium and highly dynamic. The insights gained will provide critical knowledge needed to devise wholly new approaches that will close today's technology gaps that are jeopardizing the successful completion of EM's mission in a timely and cost-effective manner. It is imperative to invest in fundamental science now to ensure EM's success.

References

BESAC – Basic Energy Sciences Advisory Committee. 2015. *Challenges at the Frontier of Matter and Energy: Transformative Opportunities for Discovery Science*. US Department of Energy, Washington, DC.

SEAB – Secretary of Energy Advisory Board. 2014. *Report of the Task Force on Technology Development for Environmental Management*. US Department of Energy, Washington, DC.

APPENDIX A – TECHNOLOGY AND APPLIED R&D NEEDS FOR ENVIRONMENTAL MANAGEMENT

Technology and Applied R&D Needs for Environmental Management

Resource Document for the Workshop on Basic Research Needs for Environmental Management

June 2015

Technology and Applied R&D Needs for Environmental Management

Resource Document for the Workshop on Basic Research Needs for Environmental Management

June 2015

Contents

Figures

Tables

Acronyms and Abbreviations

ARP	Actinide Removal Project
CSM	conceptual site model
CSSX	caustic-side solvent extraction
DOE	US Department of Energy
DWPF	Defense Waste Processing Facility
EM	Office of Environmental Management
EPA	US Environmental Protection Agency
HLW	high-level waste
HS	Hanford Site
LAW	low-activity waste
MCU	Modular Caustic-Side Solvent Extraction Unit
MST	monosodium titanate
MTHM	metric tons of heavy metal
NGS	Next-Generation Solvent
NRC	National Research Council
ORR	Oak Ridge Reservation
R&D	research and development
SEAB	Secretary of Energy's Advisory Board
SRS	Savannah River Site
SWPF	Salt Waste Processing Facility
TRU	transuranics
WTP	Waste Treatment and Immobilization Plant

Executive Summary

The US Department of Energy's (DOE's) Office of Environmental Management (EM) faces a cleanup mission resulting from World War II and Cold War legacy that involves ~302 million liters of radioactive waste stored in ~230 tanks, stabilization of more than 2,000 metric tons heavy metal of spent nuclear fuel, miscellaneous wastes including 1,900 cesium and strontium capsules, and remediation of contaminated environments that include 6.5 trillion liters of contaminated groundwater and 40 million cubic meters of contaminated soil and debris (DOE 2015a).

EM estimates that addressing these problems will take at least 50 years and cost $300 billion or more. A recent report by a task force for the Secretary of Energy's Advisory Board (SEAB 2014) suggests that the needed technologies to safely and effectively accomplish this mission will not be available. Consequently, the SEAB task force recommended that DOE increase its investments in research and development (R&D) to support the cleanup mission. One aspect of this increase is a fundamental research program tailored to the EM mission that enables new knowledge and capabilities. This new knowledge should be coupled with other investments such as a technology development program focused on improving the efficiency and effectiveness of existing cleanup processes and a high-impact technology development program that pursues technologies for processing radioactive wastes, generating waste forms, and remediating the subsurface.

In response to the SEAB's recommendation, DOE's Office of Science will convene a workshop in July 2015 to engage the scientific community in defining research opportunities that can support EM's mission needs. At this workshop, scientists from the national laboratories, academia, industry, and other organizations will discuss gaps in scientific knowledge that, if filled, could significantly advance deployment of technologies for EM.

This Factual Document is written to prepare participants for the workshop. It provides an overview of current cleanup challenges that EM faces and describes the current status of technologies available to address these challenges. As requested by DOE, the focus of this document includes the following technical areas:

- Waste stream characterization, transformation, and separation;
- Waste forms; and
- Contaminant fate and transport in geological environments.

For each of these technical areas, this document describes the technological challenge, current status of the technology, and barriers to improved and accelerated cleanup.

BACKGROUND

During World War II and the Cold War, the DOE and its predecessor agencies produced significant quantities of materials for the nation's arsenal of nuclear weapons. This large-scale production involved many processes that were conducted in multiple government-owned facilities distributed across the United States. Processes included uranium mining and milling; uranium enrichment; fuel and target fabrication; irradiation in nuclear reactors; chemical separations; production of uranium and plutonium oxide, alloys, and other metallic products; and management of the wastes associated with these processes. Because of the significant quantities of nuclear weapons materials generated for national defense, these large-scale industrial activities produced a tremendous quantity of wastes in many forms. In addition, there were intentional and accidental releases of radioactivity and hazardous materials to the environment. When nuclear weapons production ceased in the late 1980s and early 1990s, the production facilities owned by DOE were largely closed, resulting in a number of buildings and other structures requiring deactivation and decommissioning. These activities added to the monumental quantity of wastes and scrap materials resulting from the legacy of the Cold War. While at least 29 states were home to one or more sites that made up the nationwide nuclear weapons complex (DOE 1997), the states that today are left with the largest quantities of legacy materials and facilities are South Carolina (Savannah River Site), Tennessee (Oak Ridge Reservation), and Washington (Hanford Site).

To attempt to address the mounting challenge presented by the legacy wastes, DOE created the Office of Environmental Restoration and Waste Management in 1989. This office had four primary focus areas:

- Management of high-consequence nuclear materials and nuclear facilities, such as the nuclear reactors and radiochemical reprocessing plants that were no longer needed for the production of weapons-grade plutonium.
- Management of many different varieties and large volumes of waste, including highly radioactive wastes stored in waste tanks, other intermediate and low-level radioactive wastes, and hazardous wastes. In addition, this office was responsible for managing wastes generated from nuclear reactor research and basic science projects as well as some waste generated by the commercial nuclear power industry under certain circumstances.
- Restoration of sites contaminated from past industrial practices, including remediation of contaminated soil, surface water, and groundwater; deactivation and decommissioning of surplus process buildings, nuclear reactors, and chemical separation plants; and exhuming large quantities of waste buried in belowground pits and cells.
- Technology development to support activities in the first three focuses areas.

At its inception, officials at the Office of Environmental Restoration and Waste Management recognized that technology development would be essential to achieve its mission. Cleanup technologies for the specialized environmental problems associated with radioactive contamination and other unique aspects of DOE’s legacy wastes were quite limited. There were also limited treatment, processing, and disposal technologies for the wide variety of nuclear waste materials. As such, DOE was driven to invest in technological innovation. During the first decade of operation, R&D investments were greater than 5 percent of this office’s annual budget, as shown in Figure 1 (Rimando 2015).

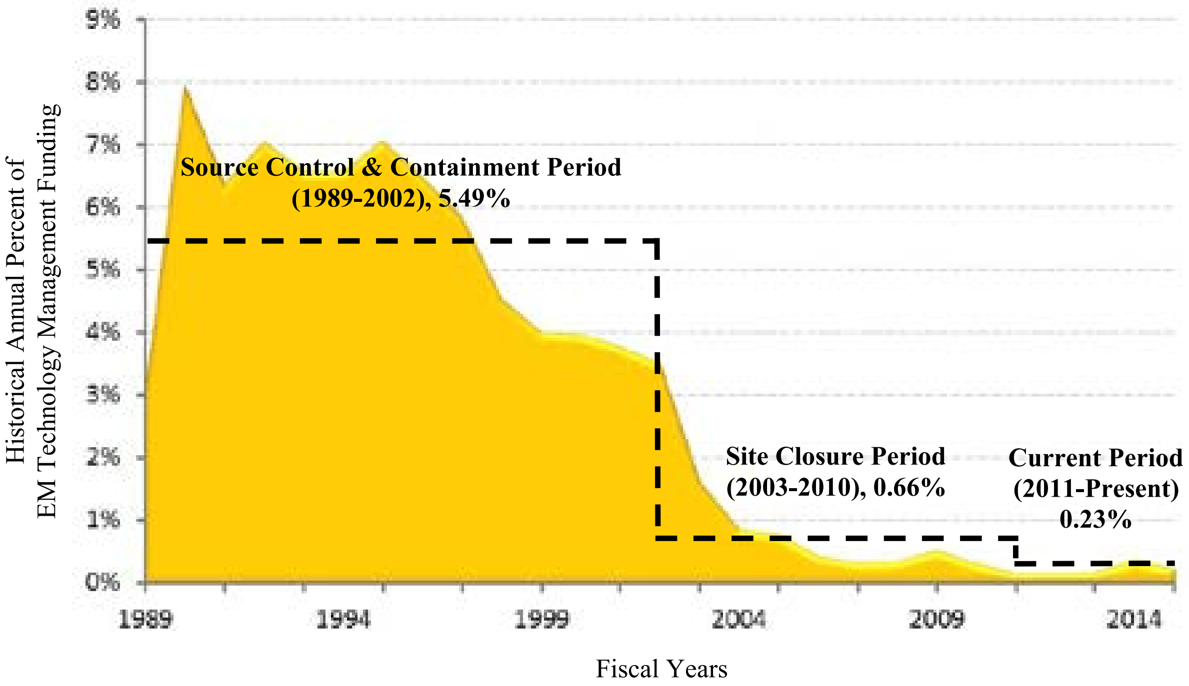


Figure 1. Historical EM Investment in Technology Development and Deployment. Image courtesy of DOE (2015c).

These earlier investments resulted in development and deployment of technologies that enabled significant progress in reducing the total environmental legacy from approximately 2003 to 2010. During this time, EM shifted its emphasis towards site closure (i.e., completing cleanup at a particular facility) and on footprint reduction (i.e., tactically completing cleanup within a particular facility to enable a reduction of the overall legacy and DOE liability). After spending more than $150 billion, the cleanup of 91 of the 107 major sites has been completed. Much of this cleanup progress and many of the innovations realized during this period were the direct result of R&D investments from 1989–2003, coupled with the creativity of site contractors in their efforts to reduce costs and accelerate schedules. But many of these sites were small and only slightly contaminated; the more difficult cleanup challenges still remain. Furthermore, this shift in focus towards technology deployment reduced R&D investments for further cleanup innovation to less than 1 percent by 2004 (see Figure 1).

Today, EM faces the cleanup of 16 remaining sites that present significantly greater difficulty and higher risk than previously experienced. In fact, the remaining work represents some of the most complex and technically challenging cleanup efforts in the world. This includes approximately 333 million liters of radioactive wastes stored in tanks that must be stabilized by producing effective waste forms for eventual disposal. Additional problems include the need to remediate large volumes of groundwater contaminated with radionuclides and other hazardous constituents. Figure 2 is a breakdown of EM's fiscal year 2015 enacted budget across its mission areas (Rimando 2015), which is an indication of its priorities. For this year, 35 percent of the EM budget is for radioactive tank waste stabilization and disposition, which reflects EM's current highest priority mission area. Note that technology development and deployment is funded at over $13 million as part of Program Management, which accounts for about 0.2 percent of the total EM budget.

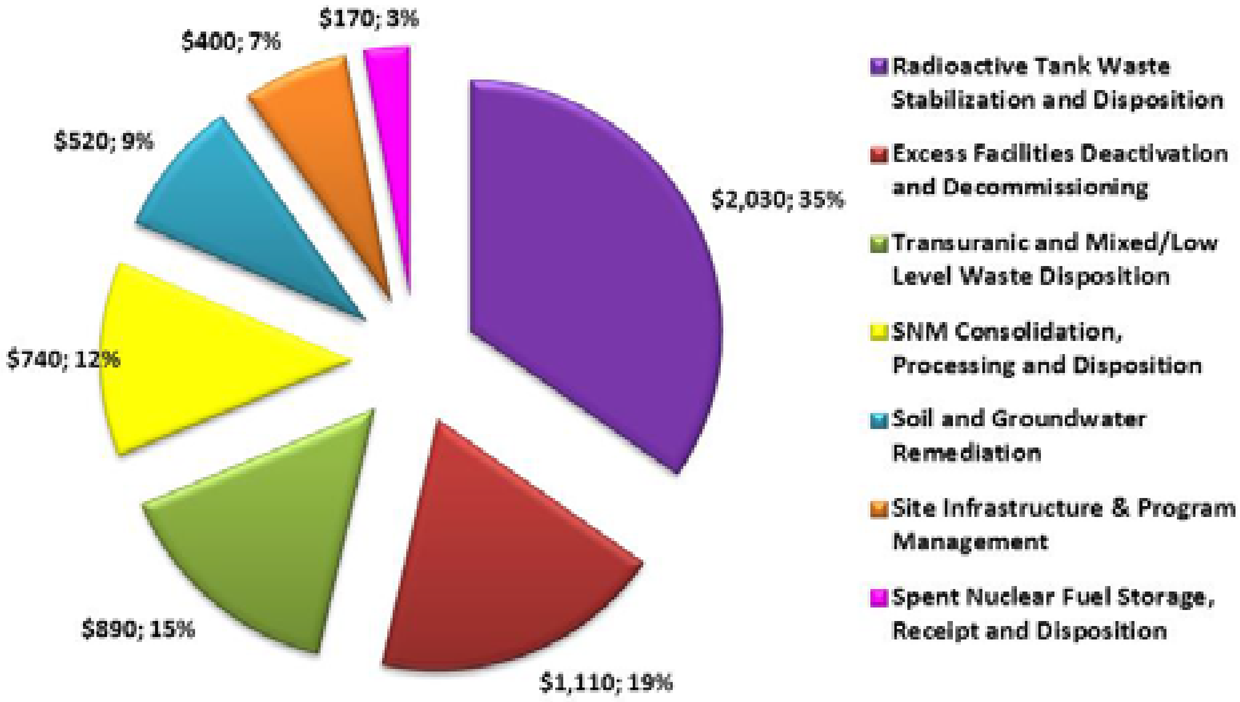


Figure 2. Distribution of Fiscal Year 2015 Budget ($5,681 Million) among EM Mission Areas. Image courtesy of DOE (2015c).

The scope of remaining technical challenges and their associated costs are indeed staggering. In projections of future costs, DOE estimates approximately $200 billion will be needed over the next decade to allow EM to comply with existing cleanup agreements and regulations (i.e., $20 billion per year for the next 10 years). As shown in Figure 3 (Michalske 2014), if this funding were available, the cleanup is projected to be completed around 2060. However, this funding level (sometimes referred to as the "compliance budget") is well above the average funding allocated to EM in recent years. Assuming a more realistic EM funding level of $5–6 billion per year, DOE will likely face noncompliance to consent orders and agreements governing cleanup. These scenarios will only increase costs further and delay completion of cleanup.

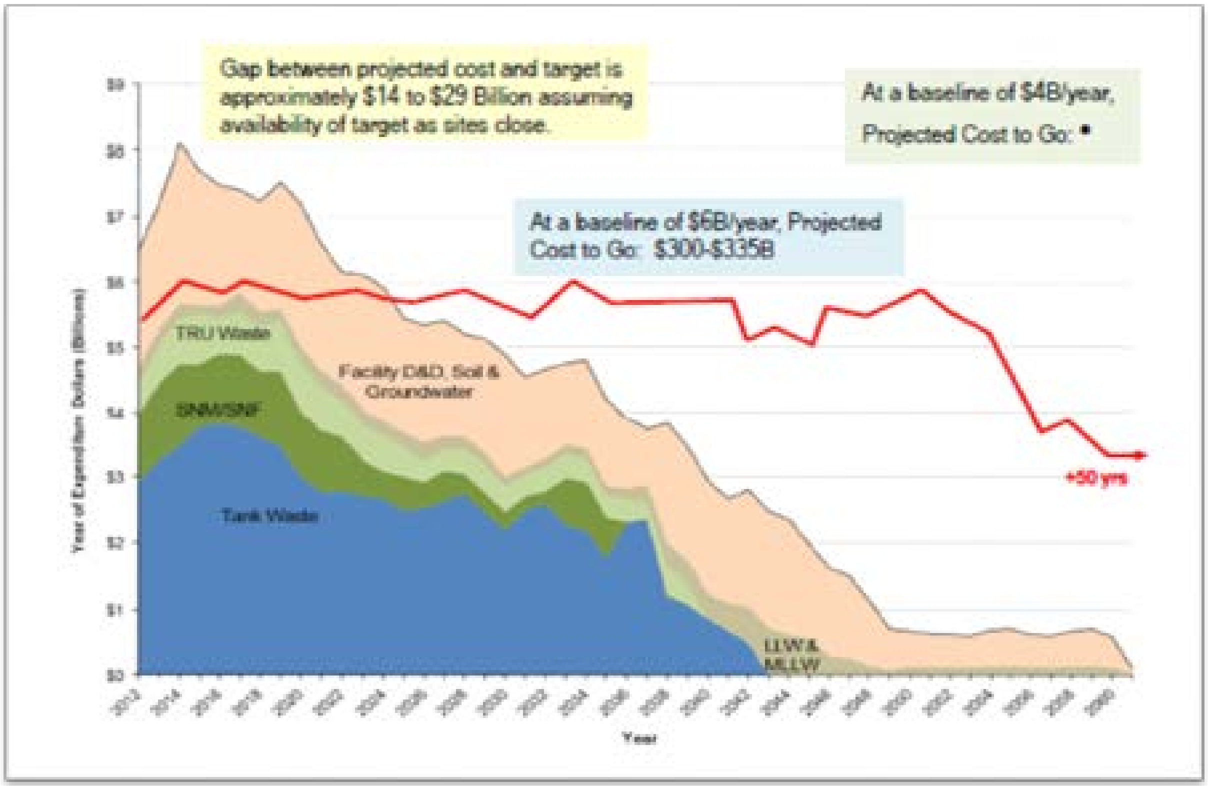


Figure 3. Projected EM Lifecycle Costs. Image courtesy of Advanced Research Project Agency for Environmental Management.

This total increase in cost is primarily due to the necessity of maintaining aging infrastructure beyond 2060, which consumes an increasing fraction of the available funds, leaving less money for the actual cleanup work. With a baseline budget of $6 billion per year, the incremental cost for completion of the work might require cumulative expenditures in future years on the order of $300–335 billion and cleanup would extend for many decades after 2060. Furthermore, because of the lack of investment in R&D, it is not clear that the technologies needed to safely and effectively accomplish the cleanup will be available (SEAB 2014).

In 2014, the Secretary of Energy formed a task force to investigate this situation and report recommendations to enable EM to meet its cleanup obligations. The primary observation of the task force is that current investment in R&D to support the EM mission is far too low (SEAB 2014). As noted above, current EM investment technology development is approximately 0.2 percent of its total budget, but successful completion of cleanup likely will require significant new technology. The task force recommended that EM increase its investments to approximately 3 percent of its annual budget. Such an investment would enable advances in science and technology and result in cost reductions, improved safety, and more effective cleanup, and accelerate EM's ability to accomplish its mission. Clearly, this will serve the American public.

The task force further recommended that EM structure its R&D investments around three strategic elements: (1) an incremental technology development program focused on improving the efficiency and effectiveness of existing cleanup processes; (2) a high-impact technology development program that pursues technologies that are outside the day-to-day program—targeting solutions with the promise of breakthrough improvements; and (3) a fundamental research program tailored to the EM mission that enables new knowledge and capabilities and that can be brought to bear on the EM challenges. Without such an investment, the task force concluded that EM will be unable to meet its commitments safely and on schedule. The task force urged DOE to take immediate and specific actions to address the many inherent technical risks and to execute the EM mission in a safe and efficient manner without further delay and added costs.

To address the third strategic element recommended by the SEAB task force, the Office of Science is planning a workshop for July 2015 to define basic research needs that can guide a fundamental research program. To tailor the research needs towards the EM mission, scientists from the national laboratories, academia, industry, and other organizations will gather at the workshop to discuss the current gaps in the deployment of technologies. This Factual Document is written to prepare participants for the workshop; it provides an overview of the current cleanup challenges that EM faces and describes the current status of technologies available to address these challenges. As requested by DOE, the focus of this Factual Document includes the following technical areas:

- Waste stream characterization, transformation, and separation;
- Waste forms; and
- Contaminant fate and transport in geological environments.

For each of these technical areas, this document describes the technological challenge, current status of the technology, and barriers to improved cleanup efficacy and acceleration of cleanup. This document does not suggest fundamental research that could reduce the barriers; instead, those recommendations and suggestions for fundamental research to bridge the technology gaps will be developed at the workshop.

WASTE STREAM CHARACTERIZATION, TRANSFORMATION, AND SEPARATIONS

Background

EM has approximately 333 million liters of liquid waste stored in underground tanks. The current DOE estimated cost for retrieval, treatment, and disposal of this waste is approximately half of the remaining EM estimate of $187–223 billion to be spent over several decades. The highly radioactive portion of this waste, located at the Savannah River and Hanford Sites, must be treated, immobilized, and prepared for shipment to a waste repository.

EM has invested in excess of $15 billion to develop processes to treat the high-level wastes (HLW) at the Savannah River and Hanford Sites. Currently, there are two operating treatment plants at the Savannah River Site with one under construction. In addition, a complex of facilities is under construction to process the tank waste at the Hanford Site. A brief summary of the facilities at these two sites is presented below.

Defense Waste Processing Facility

The Defense Waste Processing Facility (DWPF) was designed and constructed to process the sludge portion of the Savannah River Site HLW in preparation for vitrification. The sludge is the resultant slurry produced when spent acid was neutralized during weapons material production. The sludge, while comprising only about 10 percent of the volume in the tanks, contains about half of the radioactivity and most of the long-lived radionuclides. Construction of DWPF began in late 1983, with full operations initiated in March 1996. To complete its waste vitrification mission, DWPF is projected to produce approximately 7,800 canisters. To date, DWPF has processed over 60 percent of the Savannah River Site sludge inventory, equaling over 4,000 canisters of glass.

Actinide Removal Project/Modular Caustic-Side Solvent Extraction Unit

The Actinide Removal Project (ARP) is designed to remove radioactive contaminants, such as plutonium and strontium, from radioactive salt solutions stored at the Savannah River Site. Monosodium titanate (MST) is first added to the salt solutions and then radioactive contaminants that have absorbed on the MST particulates are removed from solution by filtration. These radionuclide-containing MST particulates are then transferred to DWPF for vitrification. The remaining filtered salt solution is then sent to the Modular Caustic-Side Solvent Extraction Unit (MCU) for further processing. The MCU employs a solvent extraction process to remove highly radioactive cesium from the salt waste solution stream. The extracted cesium is sent to DWPF for vitrification. The remaining decontaminated salt waste solution is transferred to the Saltstone Production Facility to be mixed with dry cement-like materials to form a grout for onsite disposal in engineered vaults. These interim salt disposition efforts at the Savannah River Site have successfully processed more than 18 million liters of salt waste.

Salt Waste Processing Facility

The Salt Waste Processing Facility (SWPF) is under construction at the Savannah River Site and is designed to complete processing of the liquid fraction of the Site's HLW. The SWPF will employ two processes: the first will remove and concentrate radioactive strontium and the actinides using sorption onto MST particulates, followed by filtration to form sludge; the second will strip the cesium from the bulk salt waste solutions using a calixerene-based solvent extraction process. The "sludge and strip" effluent from the SWPF, containing concentrated strontium, actinides, and cesium wastes, will be sent to DWPF for vitrification. The decontaminated salt solution that remains after removal of the highly radioactive constituents will be sent to the Saltstone Processing Facility for immobilization in a grout mixture and disposal in grout vaults at the Savannah River Site.

Waste Treatment and Immobilization Plant

The Waste Treatment and Immobilization Plant (WTP), which will be the world's largest and most complex radioactive waste treatment plant, will use vitrification to immobilize most of the Hanford Site tank wastes. WTP will encompass three primary treatment processes: pretreatment, HLW vitrification, and low-activity waste (LAW) vitrification. Pretreatment will separate the tank waste into two streams. The bulk of the radioactivity is concentrated into an HLW stream, which will be immobilized in a borosilicate glass waste form and transported for permanent disposal in a geologic repository to be selected in the future. The LAW stream will also be immobilized in borosilicate glass. Both forms will be stored.

Current Approaches to High-Level Radioactive Wastes

Waste tanks at Hanford and Savannah River Sites contain liquids and precipitated solids (sludge) composed of a complex mixture of chemicals in extreme environments of high pH and high radioactivity. Further, high-activity radionuclides are present in very low concentrations, presenting even more challenges for effective separations of waste components. Finally, flammable, radiolytically generated gases are found in both the headspace of the tanks and in the sludge at the bottom of the tanks. Therefore, remediation of these tanks requires specialized system-level approaches for separating tanks contents in preparation for long-term disposal. Before, during, and after processing these wastes, analytical techniques are needed to identify and quantify the various chemical components. In the following sections, current capabilities for tank waste processing, separations, and characterization are outlined.

Pretreatment of Tank Wastes

Tank wastes at both the Hanford and Savannah River Sites are initially separated into two waste streams: HLW, which contains the bulk of the insoluble transuranic species (TRUs); and LAW, which contains the bulk of the water-soluble materials. This initial solid-liquid separation step is followed by chemical (caustic or oxidative) leaching and waste slurry washing of the HLW to remove aluminum, chromium, and other nonradioactive materials that interfere in the subsequent vitrification process. Several variations on separation processes are being evaluated for treatment of liquid HLW, including the integrated salt disposition process, salt waste process, and small column ion-exchange process at the Savannah River Site. Each of these processes has a solid-liquid separation process that limits its throughput.

Crossflow filtration is a key component of these pretreatment processes, as it produces clarified streams for further processing by either ion exchange or solvent extraction. In these processes, the separation of actinides from the clarified liquids is achieved simultaneously. Applications of crossflow filtration include the West Valley Demonstration in New York, the Oak Ridge Radiochemical Engineering Development Center, and the Savannah River Site ARP. At the Savannah River Site, this technique will be used to process the majority of the supernate through either SWPF or ARP. Extensive testing of crossflow filtration has been performed in support of planned use at WTP, including more than 10 actual waste demonstrations and approximately quarter-scale pilot testing. All of these tests have demonstrated that crossflow filtration produces clarified process streams suitable for treatment by ion exchange.

One drawback of crossflow filtration is the fouling of the filter elements with solids. Fouling lowers filter throughput and significantly impacts the efficiency and schedule of pretreatment operations. Techniques to restore filter performance, such as cleaning or replacement, are limited by radiological exposure risks. Further complicating the use of this filtration method is that the highly variable waste feeds hinder assessment of the potential for fouling at the plant scale (Daniel et al. 2011; Geeting and Hallen 2005; Herman et al. 2011; Nash et al. 2003; Russell et al. 2009; Shonewill et al. 2002).

Sludge Processing

Waste tanks at both the Savannah River and Hanford Sites contain significant quantities of HLW sludge. Current approaches for treatment are optimized solely for the chemical separation of LAW components from HLW solids without regard to the full range of physical and chemical properties of this complex material. As a result, waste transfer, treatment, and other handling operations used to process tank wastes are subject to reduced throughput and operational shutdown as a result of uncontrolled and unpredictable phenomena, such as bulk waste rheology and agglomerate structure and density. Understanding these various physical and chemical properties of waste sludge is needed to avoid impacts on sludge processing.

Radiochemical Separations

Separation of hazardous waste tank materials falls into two categories: radiochemical and bulk non-radiochemical components. Two large-scale projects are underway to carry out radiochemical separation processes at WTP and SWPF. The key pretreatment unit operations include radionuclide separations (^{137}Cs, ^{90}Sr, TRU elements) and removal of bulk nonradioactive components by washing and leaching operations. Many methods for separation of these radionuclides have been explored and demonstrated over the last 60 years. Specific requirements in terms of regulatory limits on LAW differ between the two sites, as do the compositions of the waste. These differences have necessitated different separation technologies for some radionuclides at each site. The following sections outline the various technologies that have been demonstrated for cesium, strontium, and transuranic elements as well as ^{99}Tc.

Cesium Separation

The very high concentration of sodium as compared to the concentration of high-activity ^{137}Cs in HLW requires separation approaches with a high selectivity for cesium to minimize the volume of the resulting cesium-containing stream. In many cases, this problem is exacerbated (especially at the Hanford Site) by relatively high potassium concentrations; achieving high cesium selectivity over potassium is even more difficult than for sodium. In addition, the overall chemical composition and properties of HLW make for an exceptionally challenging environment for many separations processes. In addition to the need for separation approaches to be highly selective, they must also be stable under conditions of high alkalinity and radiation.

The removal of cesium from alkaline wastes stored at Hanford and Savannah River Sites has been studied for over 50 years (Schulz et al. 1987). A number of technologies have been considered for removing ^{137}Cs from alkaline tank waste liquids, including precipitation, selective dissolution, crystallization, ion exchange (both elutable and nonelutable), and solvent extraction.

Solvent extraction is the current preferred technology for cesium removal at the Savannah River Site, while the Hanford Site is pursing elutable ion exchange. The Savannah River Site implemented a solvent extraction process, known as caustic-side solvent extraction (CSSX) at MCU in 2008 (Brown 2010), which could not originally handle the high concentrations of potassium found in Hanford Site wastes. This facility was built as a pilot for the larger SWPF, currently under construction. The CSSX process was developed to remove ^{137}Cs from alkaline tank waste solutions (Bonnesen et al. 2000). The CSSX process uses calix[4]arene-bis(4-tert-octylbenzo-crown-6), referred to as “BOBCalixC6,” as the extractant. Because this molecule binds cesium ions far more strongly than sodium ions, it is able to selectively extract cesium into the organic phase, thereby separating it from the other waste components which remain in the aqueous phase. The CSSX solvent also contains a modifier, to improve the solubility of the extractant, and tri-n-octylamine, which mitigates the effects of anionic impurities in the solvent (Bonnesen et al. 2003). These components are dissolved in a hydrocarbon diluent (Isopar™ L from ExxonMobil Chemical, Spring, Texas). The MCU design basis assumes the cesium decontamination factor is at least 12; however, the seven extraction contactors routinely operate an order of magnitude better.

Work has recently been performed to improve the CSSX process at the Savannah River Site and possibly extend its application to Hanford Site. Researchers at Oak Ridge National Laboratory have developed a new solvent system, known as Next-Generation Solvent (NGS), which was recently deployed in the MCU process at the Savannah River Site, replacing the current CSSX system (see Figure 4, Moyer et al. 2011). The NGS system uses a new extractant, 1,3-alt-25,27-bis(3,7-dimethyl-1-oxy)calix[4]arene-benzocrown-6, referred to as “MAXCalix,” which has much higher solubility in the Isopar™ L diluent, allowing it to be deployed at a higher concentration in the solvent (Moyer et al. 2011). The increased solubility of the extractant not only allows for higher cesium extraction, but also improved hydraulics, as the modifier concentration can be decreased. Flowsheet design calculations with the data obtained from both simulant and real waste testing showed that replacing the CSSX solvent with NGS in the current MCU equipment configuration could raise the minimum decontamination factor to more than 40,000, with a likely increased waste feed processing rate. The MCU has already begun operation using the NGS technology.

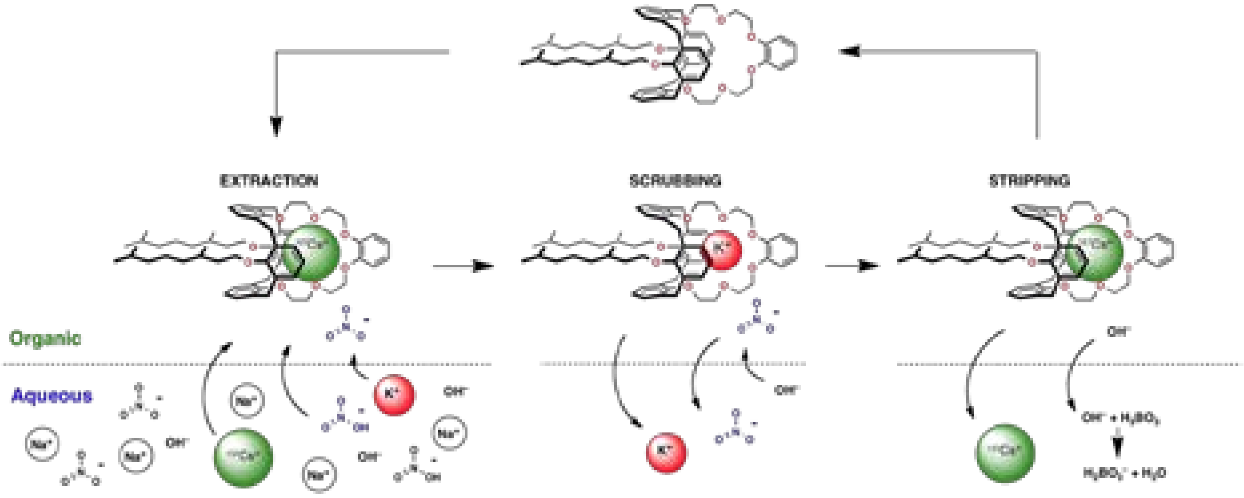


Figure 4. Next-Generation Solvent System (Moyer et al. 2013). Image courtesy of Oak Ridge National Laboratory.

A variety of polymeric organic resins and inorganic ion-exchange materials have been evaluated for removing ^{137}Cs from alkaline liquid wastes at the Hanford and Savannah River Sites (Bray et al. 1993 and 1995; Brown et al. 1996; Wester et al. 2003). During the initial design of WTP, cesium ion exchange using SuperLig® 644 was selected as the baseline technology for removing ^{137}Cs from the LAW stream (Kurath et al. 1999 and 2000). SuperLig® 644 is a proprietary material marketed by IBC Technologies (American Fork, Utah). The SuperLig products consist of selective macrocyclic ligands covalently bound to solid supports (Izatt et al. 1999). More recently, a spherical resorcinol-formaldehyde resin has been selected to remove ^{137}Cs from LAW at the Hanford Site (Fiskum et al. 2006a-c; Thorson 2008). The resorcinol-formaldehyde resin is a condensation polymer formed by reaction of the deprotonated form of resorcinol with formaldehyde. After loading, the resin is eluted with dilute nitric acid to recover the cesium; the resin can then be reused for multiple loading and elution cycles. Decontamination factors on the order of 100,000 have been achieved in testing with this resin.

In contrast to the elutable organic resorcinol-formaldehyde resin, crystalline silicotitanate is a nonelutable inorganic ion exchanger that displays remarkable selectivity for cesium in highly alkaline solutions with high salt concentrations as well as from neutral and acidic solutions. Crystalline silicotitanate was evaluated as a possible technology for cesium removal in the SWPF; however, solvent extraction was eventually chosen as the preferred technology for this facility (Dimenna et al. 2001). More recently, this technology has been examined for use in smaller, more modular designs (Walker et al. 2004). One system that received consideration is known as small column ion exchange, which uses an ion-exchange column placed inside a tank riser. Another in-riser deployment consists of pumps and rotary microfilters to remove entrained solids and pump the retrieved waste through the ion-exchange column(s). A third module consists of a grinder to reduce the particle size of the spent crystalline silicotitanate and render it compatible with downstream processing when mixed with sludge being readied for vitrification. Substituting the elutable spherical resorcinol-formaldehyde as the ion-exchange media has been considered.

Strontium and Actinide Separations

For removing strontium and actinides from the Savannah River Site waste, MST, an inorganic sorbent material (see Figure 5, Peters et al. 2010), has been selected. This material was first developed by researchers at Sandia National Laboratories (Dosch 1978; Lynch et al. 1976). The synthesis was later modified by researchers at Savanah River National Laboratory to optimize performance, producing spherical particles with an average size of 1–10 microns (Hobbs et al. 2005; Peters et al. 2006). In 2001, MST was selected as the strontium and actinide separation technology for SWPF; it was subsequently selected for use in the ARP as well. The ARP facility was started up in conjunction with the MCU facility. The ARP facility involves vigorous mixing MST with the waste in a batch contact process, followed by crossflow filtration to remove the MST and any entrained sludge solids (Peters et al. 2010). A peroxide-modified version of MST has shown increased kinetics for strontium and plutonium removal over the MST. The peroxide-modified MST is prepared by treating the MST with hydrogen peroxide to form a peroxotitanate (Nyman et al. 2006). This material is being considered as a possible replacement for MST, allowing use of smaller quantities of sorbents and shorter contact times to achieve the same level of decontamination.

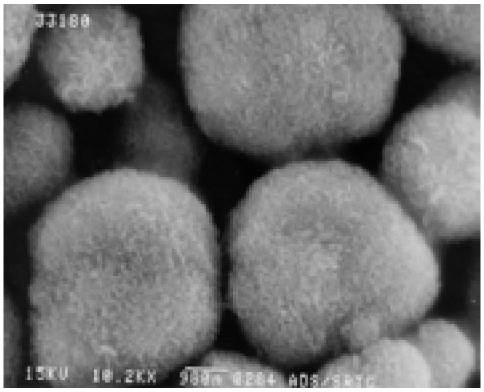


Figure 5. Photomicrograph of MST. Image courtesy of Hobbs et al. (2006). With permission of Wiley.

The complexed species of strontium, plutonium, and americium present in Hanford Site wastes do not readily sorb onto MST; therefore, a different separation method is required. In a process demonstrated for separating the ^{90}Sr and TRU components from the 241-AN-102 and 241-AN-107 wastes (Hallen et al. 2002; Nash et al. 2003; Wilmarth et al. 2001), ^{90}Sr is removed by adding strontium nitrate to precipitate strontium carbonate following a caustic adjustment step. This step is followed by adding a sodium permanganate solution that forms a precipitate of manganese oxides or hydroxides. The TRU components of the waste follow the precipitated manganese phase. The process has been optimized so that strontium nitrate and permanganate addition are minimized with no added hydroxide or use of elevated temperatures.

Technetium Separation

Technetium-99 is a long-lived radionuclide that is present in tank waste in both the sludge and supernate phases. In most cases, the technetium is present in the supernatant as the pertechnetate ion (TcO_4^-); however, there has been varying amounts of a non-pertechnetate species identified in some Hanford Site tank waste samples that has yet to be fully characterized. Because pertechnetate is extremely mobile in the environment, its presence is often a key risk driver in performance assessments for waste form disposals. Ion-exchange processes have been extensively explored for pertechnetate removal from HLW; however, these technologies are ineffective at removing the non-pertechnetate species. DOE conducted extensive testing of commercial and developmental ion-exchange materials for separating various radionuclides from Hanford Site tank wastes; acceptable ^{99}Tc batch-distribution ratios were demonstrated for a number of materials (Marsh et al. 1995).

The WTP project conducted extensive testing of SuperLig® 639 resin (Johnson et al. 2000). Laboratory-scale and pilot-scale column tests were conducted using simulants and actual tank waste samples (King et al. 2001; McCabe et al. 2000). Chemical and radiation stability testing of SuperLig® 639 resin has also been conducted. These tests demonstrated that technetium could be effectively removed from most Hanford Site HLW tanks; however, removal efficiency was poor for the tanks that contained high concentrations of complexants and alternative removal and disposal technologies would be needed.

Separation of Bulk Nonradioactive Components

Dissolution of a number of nonradioactive components of HLW is essential to waste processing including gibbsite, boehmite, chromium oxide/hydroxide, phosphate salts, and oxalate salts. Testing has been performed to assess the dissolution kinetics of boehmite; however, this work has resulted in semi-empirical models for boehmite dissolution and has not yet assessed gibbsite dissolution kinetics. A limited amount of work has also been done on the dissolution kinetics of chromium phases.

Two of the most prevalent materials in the Hanford Site HLW sludge include aluminum and chromium. Aluminum in the tank wastes is believed to be present in the two most common mineralogical phases: gibbsite (monoclinic $Al(OH)_3$) and boehmite (orthorhombic AlOOH). Other aluminum-containing phases present include bayerite, dawsonite, alumina silicate, and amorphous aluminum hydroxide. Studies on the speciation of chromium in Hanford Site tank sludge have indicated that chromium exists both in its +3 and +6 oxidation states, with the ratio of chromium(VI) to chromium(III) varying greatly depending on the sludge examined. Studies have shown that oxidative leaching of aluminum and chromium with sodium permanganate is highly effective, with removals of greater than 95 percent achievable. In previously washed sludge with large quantities of chromium, it was determined that chromium is generally present either in a pure chromium-oxide phase or together with aluminum. In some waste tanks, substantial iron and manganese appear to be mixed with the leachable aluminum and chromium. Despite the possibility that chromium removal might be inhibited by the presence of these un-leachable metals passivating the particle surface and making the chromium in the bulk of the sample inaccessible to oxidant, excellent removal of chromium was observed.

After the HLW is separated from the LAW liquid stream by ultrafiltration in the pretreatment facility, the concentrated HLW sludge undergoes caustic and oxidative leaching processes to dissolve and remove aluminum, chromium, and additional materials (phosphates and sulfates) that would otherwise limit HLW loading in the glass waste form. The concentrated HLW solids are sequentially caustic leached, washed, oxidatively leached, and washed once more during pretreatment. The caustic leaching dissolves the aluminum in the HLW solids. The oxidative leaching uses sodium permanganate solution to oxidize the chromium to Cr(VI) and dissolve it into a mild caustic solution. The HLW solids are concentrated after each leaching and washing operation using crossflow filtration.

Gas Retention and Release

In addition to liquid and solid components, gases are present in waste tanks. Hydrogen gas produced by radiolysis is a major concern due to its flammability and potential for explosion. Each waste tank at the Hanford and Savannah River Sites is classified with respect to hydrogen (and other gases) generation rates and purge ventilation is used to avoid buildup of flammable gases. Bubbles of hydrogen gas are also retained in the radioactive waste slurries, and this potential for retention of hydrogen gas must also be managed. The size of the bubbles is known to affect both the retention and release of hydrogen from waste in underground storage tanks and in process vessels (Gauglitz and Terrones 2002). Figure 6 shows the surface of a Savannah River Site sludge tank releasing trapped gas, with inset showing gas escaping from the sludge.

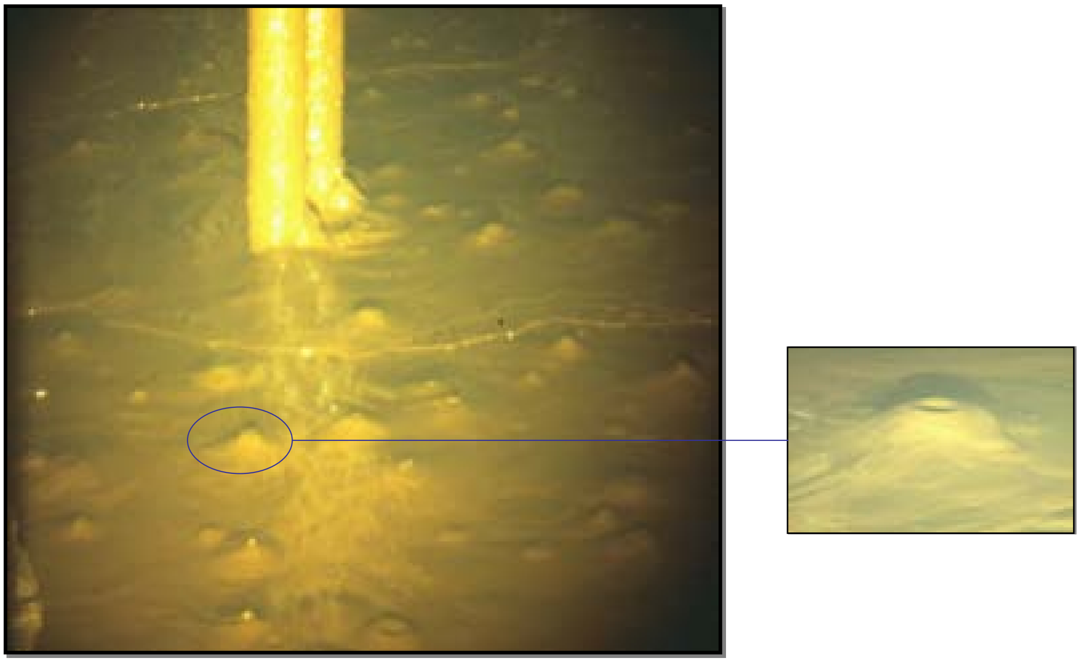


Figure 6. Surface of Sludge in Savannah River Site Tank with Inset Showing Gas Escaping from the Sludge. Image courtesy of DOE Savannah River.

Previous studies have shown that the yield stress and particle size of the slurry are two important parameters (Rassat et al. 1998) to the macroscopic properties regarding gas retention and release; however, the microstructural properties affecting gas retention and release are still not well understood.

These include particle wettability, surface tension, and parameters describing the behavior of the slurry in particular the yield stress and strength. While studies have considered the quasistatic (slow) deformation of bubbles in yield stress materials, the dynamic behavior at the microstructural level has not been explored and could perhaps reveal how the gas bubbles are actually retained. For example, the rapid release of gas bubbles via a bubble cascade mechanism is a poorly understood phenomenon that may be a significant issue for future waste retrieval and mixing activities.

Characterization of High-Level Wastes and Associated Waste Streams

Before and during waste processing and for performance assessment certification before waste tank closure and/or removal, HLW tank solutions and associated waste streams require extensive characterization. However, characterization of the materials containing radioactive species is often complicated because the analytes of interest are present at low concentrations in a complex matrix and include species with long half-lives with lower energy modes of decay. With current technologies, a significant number of steps are needed to concentrate the analytes and simplify the sample matrix to improve both analyte identification and limits of detection. Today's approaches for characterization in support of waste processing and storage are complex and time consuming, adding significant costs and time to waste remediation project schedules. Processes typically include conventional techniques such as radioanalytical counting and inductively coupled mass and emission spectroscopies. All of these techniques are sequentially performed in a radiological laboratory with few in-tank analyses performed.

For example, at the Savannah River Site analytical characterization is required for qualification of processed sludge and salt before disposal, as well as for tank closure (Oji et al. 2012a, 2012b, and 2014). As a result of the challenges outlined, analytical requirements can seriously impact the project's critical path. More daunting, however, is that the number of samples currently required for in-depth characterization; at the Savannah River Site, it is quite small in comparison to the anticipated needs once the SWPF begins full operation with the same challenge applying at the WTP. The estimated analytical costs for the Hanford Site lifecycle are on the order of hundreds of millions of dollars, for example. Thus, significant improvements in approaches and methods to support analytical characterization are critically needed to meet future processing loads at the Hanford and Savannah River Sites as well as regulatory requirements for disposal and disposition. Strategies and new concepts and technologies to understand, optimize, scale, and accelerate tank wastes and associated materials could provide significant benefit to DOE in the form of faster turnaround times, improved quality and accuracy, and significant reduction in total analytical costs.

Summary of Technological Challenges

Technology challenges exist that could provide opportunities for enormous improvements to the separation and characterization of waste tank materials.

- **Improvements in separations processes.** New approaches and materials for chelation, ion exchange, and other separation methods are needed to make separations more selective and radiation tolerant.
- **Scalable, efficient separations processes.** Scalable processes need to be designed as a system rather than a collection of sequential steps to improve efficiencies and reduce costs by bringing the solution closer to the tank or by making processes more modular in nature. It may be possible, for example, to simultaneously remove more than one target species, such as aluminum and chromium, in a single step.
- **New approaches for separating HLW and LAW**. Today's filtration devices used to separate liquids from solids are prone to clogging and, once clogged, are difficult to remediate. New materials and

architectures are needed for these filters to minimize clogging. This area could also include fundamental studies to enhance retrieval and decontamination (either radioactive or chemical).

- **Higher sensitivity, more efficient characterization techniques**. Considerable time and costs are associated with the characterization of waste materials due to the extensive sample preparation that is required to concentrate materials before analysis. Approaches are needed to rapidly prepare and characterize waste stream samples while maintaining high accuracy and precision. It would also be important to minimize sample size to reduce radiation exposure. In-line sensors to monitor plant-scale processes would also provide rapid feedback to operators of any operational issues.
- **Improved understanding of process parameters.** Rheology and speciation (e.g., agglomerate structures) in pretreatment processes are poorly understood and improvements to this knowledge could be used to increase efficiencies of separations and minimize down time. For example, methods could be devised to stabilize/inhibit precipitation of partially soluble salts during processing and prevent filters from clogging.

WASTE FORMS

Background

Radioactive waste is converted into a form that is suitable for its subsequent transportation, storage, and disposal. The resulting waste forms provide a barrier to releasing the radioactive and hazardous components to the environment. Alternatively, such as in the case of some EM-owned spent fuel, the fuel itself serves as the form for storage and eventual disposition. Technical challenges associated with waste forms center around waste form chemistry and processing and the necessity to provide an acceptable safety case to support storage and ultimate disposition. The current state of EM's waste form development efforts and challenges are captured in the following sections.

Current Approaches for Radioactive Waste Forms

Vitrification and Glass Chemistry

Waste immobilization challenges at the Hanford Site include the efficient processing of HLW and LAW into glass, the need for additional capacity for the LAW stream, and the incorporation of key chemical components into the melt and glass during vitrification. The throughput of waste at any of the potentially four vitrification plants (WTP at the Hanford Site, DWPF at the Savannah River Site, and secondary LAW plants) is determined by the following relationship:

$$\text{Throughput} \simeq \text{waste loading in glass} \times \text{melting rate} \times \text{the plant availability}$$

This throughput rate must be increased to shorten the cleanup schedule and reduce lifecycle costs.

Constraints that limit waste loading in glass are associated with processing concerns and waste form qualification requirements (Kim et al. 2011). Overly conservative constraints are the result of a lack of information on the effect of waste and glass composition on melter operational parameters (McCloy and Vienna 2010). Therefore, increasing the efficiency and lowering the risk of HLW and LAW processing will require improved scientific understanding of the materials and processes that impact waste vitrification.

Solving these challenges requires improved understanding related to physical and chemical behavior of melter feed, molten glass, solid glass, and the transitions between these states. A schematic of a melter is provided in Figure 7. The five key areas of interest are (1) melting processes and rates, (2) technetium volatility during vitrification, (3) molten salt accumulation during glass fabrication, (4) crystallization and crystal accumulation during glass fabrication, and (5) crystallization during glass cooling in the canister and durability of the final waste form.

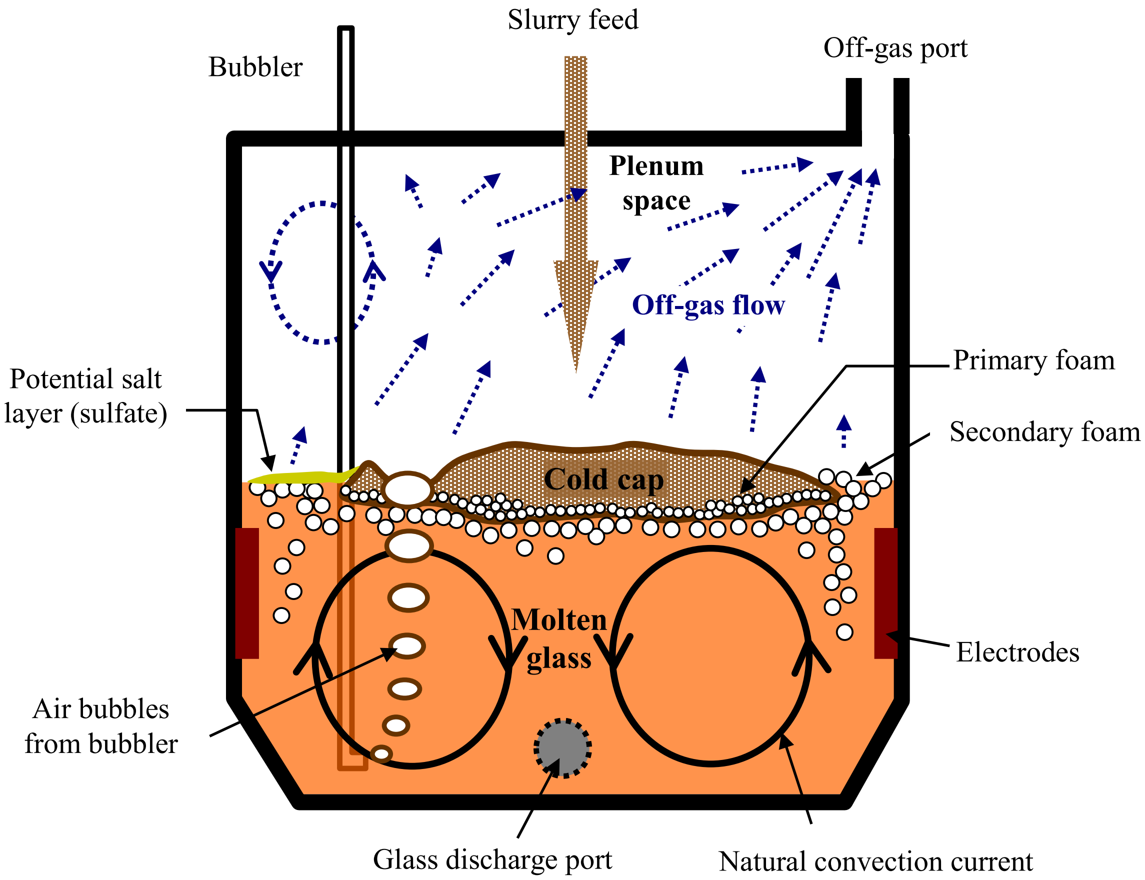


Figure 7. Cross Section of Cold-Cap Melting in Joule-Heated Melter (Kim et al. 2012). Image courtesy of Pacific Northwest National Laboratory.

Melting Rate

The melting rate is subject to a complex dependency between waste feed composition and melter operating parameters and can vary by over an order of magnitude for simulated Hanford Site HLW glass melts (typically 180 to 3200 $kg \cdot m^{-2} \cdot d^{-1}$). The HLW melter feed is slurry containing 40 to 60 wt% water. This slurry is fed onto the top of a molten glass pool where it dries to form a cold cap. Inside the cold cap, the dried feed is progressively heated and undergoes a series of reactions until it is ultimately converted into silicate melt. The feed reactions form gas, liquid, and solid intermediate phases. While the gases are released from the melter, they interact with the cold cap and may significantly impact reactions and heat transfer. The total number of reactions is large with up to 60 chemical components in the melter feed; however, a smaller number of reactions are believed to control the overall melter feed-to-glass conversion rate. In addition to the rate of reactions, the heat transfer rate to and within the cold cap limits the glass melting rate.

Technetium Volatility from the Melter

Roughly 1,500 kg of ^{99}Tc are contained in the waste tanks at the Hanford Site. This technetium will partition between the LAW (~90 percent) and HLW (~10 percent) melter feed (Serne et al. 2014). During normal melter operation, a fraction of the technetium is liberated to the gas stream primarily through cold-cap reaction. Some technetium is liberated from the melt pool; the fraction liberated from the melt pool is significantly higher during melter idling periods (Pegg 2015).

Although there is some uncertainty in the exact technetium-containing gaseous compounds responsible for the volatility, it is generally believed, based on limited data, that alkali pertechnetates are the primary gaseous species (e.g., $[Cs,K,Na]TcO_4$). Approaches are needed to maximize technetium retention in glass and minimize or eliminate the need for recycling the off-gas stream, which could greatly increase LAW processing rates and resolve the technetium management challenge (Jenkins et al. 2012).

Salt Accumulation in the Melter

Melter feeds with excess concentrations of certain anions will form a salt that accumulates on the melt surface. This salt contains primarily alkali- and alkaline-earth sulfates, chromates, pertechnetates, and halides. The salt creates potential problems associated with melter operation including the following:

- Corrosion of melter components such as bubblers, thermowells, and refractories;
- Corrosion of off-gas components by increased volatility and condensation of salt components;
- Increased volatility of technetium and cesium through partitioning into salt; and
- Formation of water-soluble salt phases containing technetium and cesium in canister glass.

Waste glass melters, including those at the Savannah River and Hanford Sites, are operated in a way to avoid salt accumulation. Avoiding salt formation in the melters is currently accomplished using conservative empirical limits on sulfur (often tabulated as trioxide) and in some cases also chromium and halides (Edwards et al. 2006; Kim and Vienna 2012; Vienna and Kim 2014).

Crystal Formation and Accumulation in the Melter

Crystal accumulation in a waste glass melter has been shown to clog the bottom drain, disrupt power to the melter, or clog an airlift pour spout. The airlift pour spout is the riser pipe that begins at the glass discharge spout indicated on Figure 7; however, it is not currently known how much of each type of crystal can be tolerated in a melter without causing processing problems or limiting the melter lifetime. A conservative limit on crystallinity was adopted by the DWPF that the liquidus temperature (T_L) must be less than 1050°C to avoid any crystals (noble metals and their oxides excluded) in the melter (Edwards et al. 2006; Fox et al. 2014). WTP has constrained the glass composition to produce less than 1 volume percent of crystals at 950°C (Vienna and Kim 2014). These constraints, particularly in the spinel ($[Fe,Mn,Zn,Ni][Cr,Fe,Mn,Al]_2O_4$) primary phase field, limit the loading of waste in glass without significantly reducing the risk of problems caused by crystals in the melter. Meanwhile, it was clearly shown by a combination of laboratory testing and melter modeling that crystal fraction and size are far better predictors of potential melter failure caused by spinel buildup than T_L or $T_{1\%}$ (Hrma et al. 2003). A review of the WTP HLW melter design and operating strategy identified crystal accumulation in the pour-spout riser as the most likely failure mode due to crystals.

Crystal Formation in the Canister and its Impact on Durability

If nepheline (ideally $NaAlSiO_4$) precipitates from HLW glass during canister cooling, it can reduce the chemical durability of the glass by removing aluminum and silicon from the residual glass at a 1:1:1 ratio with sodium (Kim et al. 1995). It will also make it difficult to predict the product consistency test response of the glass. Because the test response must be controlled and reported to meet current disposal criteria (DOE 1996), nepheline precipitation must either be avoided or the amount of nepheline formed and its impact on the product consistency test must be predicted. Because canistered waste glass will be subjected to a broad range of thermal histories, a simulated canister centerline cooling is used as a bounding thermal history to determine the risk of nepheline formation. A nepheline discriminator was developed and shown to successfully reduce the risk of nepheline precipitation in canister centerline cooling of heat-treated waste glasses (Li et al. 1997). The nepheline discriminator is based on limiting the normalized SiO_2 concentration (N_{Si}) as follows:

$$N_{Si} = g_{SiO_2} \Big/ \left[g_{SiO_2} + g_{Al_2O_3} + g_{Na_2O} \right]$$

to greater than 0.62 in the glass as shown in Figure 8. The behavior over time is dependent on glass composition and leaching conditions (pH, temperature, solution composition, etc.) (Vienna and Kim 2014). The nepheline discriminator constraint is overly conservative, however. As can be seen in the plot, several glasses with N_{Si} <0.62 do not form nepheline on slow cooling. The lower N_{Si} glasses are those with the highest waste loadings, and therefore a less conservative method of limiting nepheline precipitation is needed to both maintain acceptable glasses and allow higher waste loading.

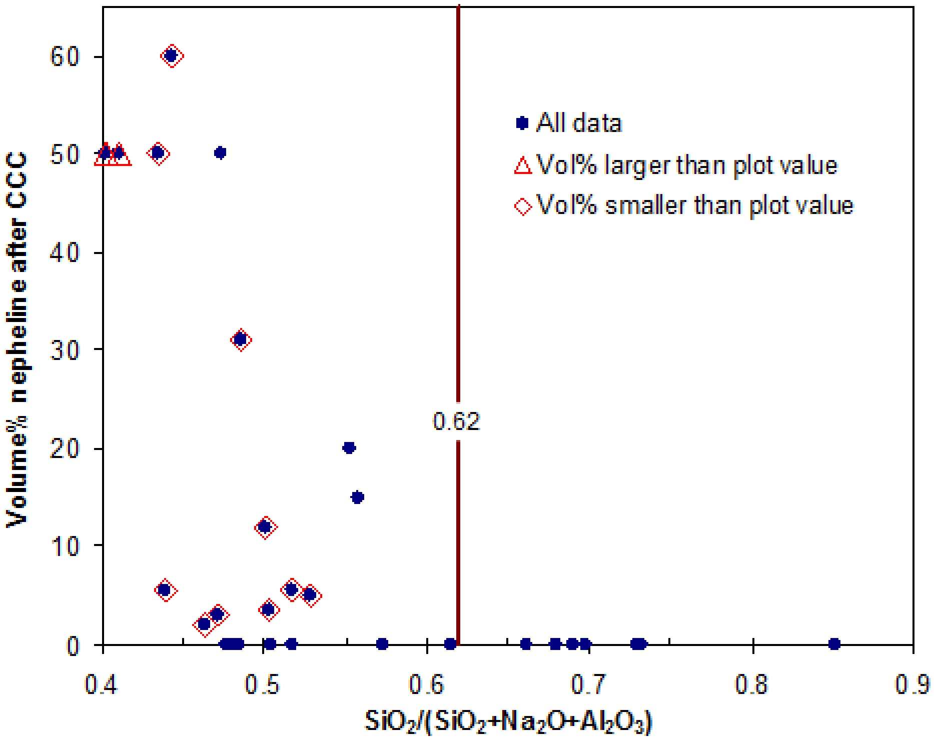


Figure 8. Nepheline Fraction in Canister Centerline Cooled HLW Glass Samples (Vienna and Kim 2014). Image courtesy of DOE Office of River Protection.

Long-Term Radionuclide Release

The primary function of the waste form is to provide a barrier to the release of radionuclides and other hazardous components to the environment during storage, transportation, and disposal. Performance expectations are controlled by regulatory, state, local, and stakeholder agreements. At least three forms requiring disposition are anticipated based on the current EM cleanup baseline: HLW glass, low-temperature waste forms (e.g., cementitious), and spent nuclear fuel.

High-Level Waste Glasses

The intent of glass waste forms is to immobilize the radioactive and hazardous components present in HLW for the extended periods associated with planned geological disposal. An extensive database along with a general understanding of the physicochemical processes that control glass weathering in various geologic disposal environments does exist (Van Iseghem et al. 2001). As glass reacts with water, several processes occur: water diffusion; ion exchange between the solution and alkali ions in the glass; hydrolysis of covalent and ionocovalent Si-O-M bonds; condensation of detached species from the glass surface; and precipitation of crystalline phases from amorphous phases and soluble species (Gin et al. 2013). Composition of the glass and conditions near the glass surface dictate the dissolution behavior of the glass. Depending on their relative solubility, the components of the glass (including the radionuclides) can dissolve into solution, stay at the glass surface in a hydrated gel layer, or precipitate as crystalline alteration phases. Under geologic disposal conditions, glass corrosion has been characterized by three kinetic regimes or stages: I, an initial high rate; II, a residual relatively slow rate; and in some instances III, an acceleration to relatively rapid corrosion after a period of slow rate (Van Iseghem et al. 2009). Figure 9 depicts these stages of glass alteration under static or slow flowing conditions. The rate drop coincides with the progressive saturation of the solution with respect to silica and/or the formation of surface layers that impede further corrosion (Grambow 1985).

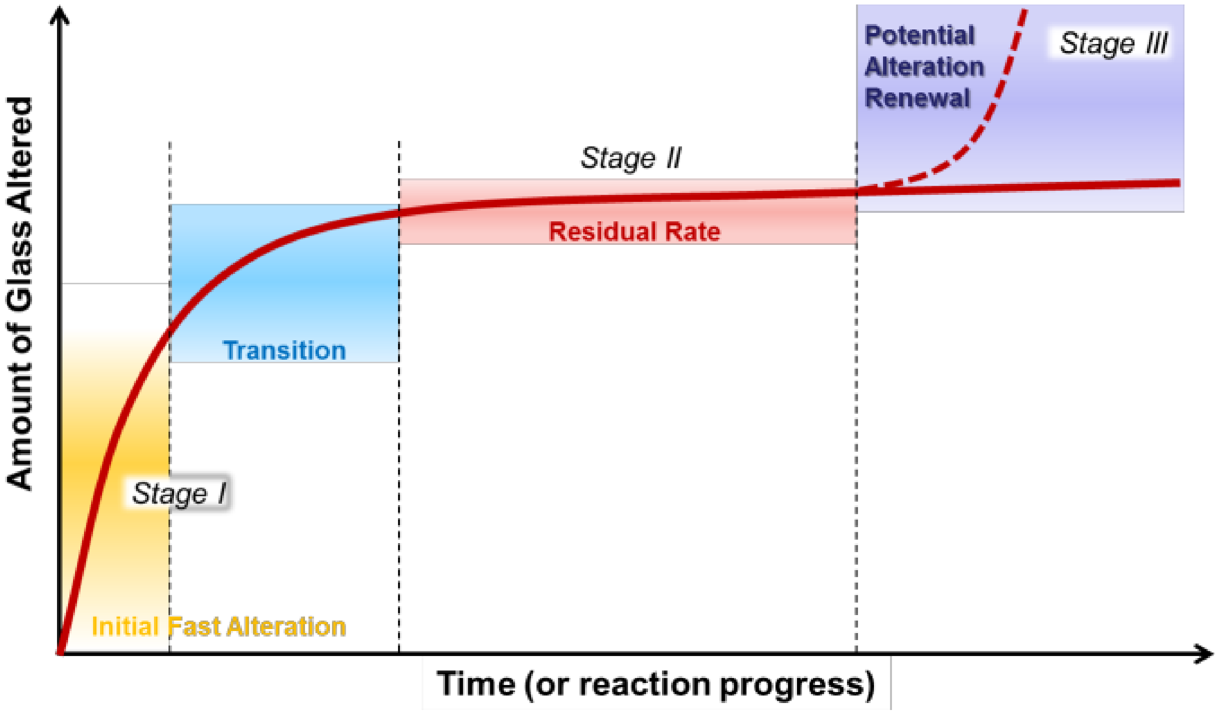


Figure 9. Stages of Radioactive Waste Glass Corrosion. Image courtesy of Vienna et al. (2013). With permission of Wiley.

Low-Temperature Waste Forms

Low-temperature immobilization forms are applicable to a wide range of DOE waste streams, including aqueous wastes (solutions and sludges), solid wastes, organic liquid wastes, debris, environmental wastes, radioactive sources, and large volume disaster waste. Low-temperature waste forms have been successfully used to produce final waste forms across the DOE complex and are also widely used internationally (Spence and Shi 2005).

Currently, DOE is using low-temperature waste forms and engineered barriers as an effective means for disposal of low-level wastes where assessments can be developed to validate waste form and disposal system performance (Flach and Smith 2013; Langton and Dukes 1984).The decontaminated aqueous waste stream resulting from pretreating HLW tank waste is classified as waste incidental to reprocessing, which can be disposed of in a near-surface facility provided that the workers, public, and environment are protected. Establishing the performance and predictability of low-temperature, low-level waste forms are essential to demonstrating their suitability for disposal.

Waste Tank Closure and In Situ Decommissioning

The accepted process for closure of HLW tanks is to remove residual waste from the tanks using remote processes (including mechanical and chemical methods) and stabilizing the tanks and immobilizing the residual contaminants with grout. The waste tank closure process reduces risks to human health and the environment by securing residual waste in the tanks, which minimizes the potential for groundwater contamination (Thomas and Dickert 2013). EM has also been developing and implementing in-tank decontamination strategies and technologies as an alternative to conventional deactivation and decommissioning and disposal actions. The general steps begin with deactivation (radiological characterization; removal of water, oils, and other hazardous liquids; and sealing lines and penetrations); physical stabilization of the below-grade portion of the structure by filling with structural grout/concrete; sealing structure openings; installing roof slab to prevent in-leakage (if necessary); and long-term monitoring, surveillance, and maintenance of the remaining above-grade structure.

Specialized grouts have been formulated for entombment of high-activity waste tanks and deactivated nuclear reactor facilities (Blankenship et al. 2012; Langton et al. 2007). The grouts used for entombment are specifically formulated to ensure the grout can flow to level prior to hardening and with a lower pH to minimize chemical reaction with structural components. The use of cement-based materials for long-term disposition of facilities is supported by detailed performance assessments.

Spent Nuclear Fuel

Currently, EM manages approximately 2,400 metric tons of heavy metal (MTHM) of spent nuclear fuel, including approximately 2,130 MTHM at the Hanford Site and about 30 MTHM at the Savannah River Site (DOE 2015b). This fuel is production reactor and research reactor fuel of a multitude of designs (fuel core, cladding, geometry), including repatriated US-origin and certain non-US-origin enriched uranium fuel and US domestic reactor fuel of various enrichments. An alternative to reprocessing this fuel is to directly dispose of it permanently in a geologic repository. That is, the fuel itself is the waste form in a disposal setting. The fuel would likely be placed in a canister or other packaging to facilitate handling.

In establishing spent nuclear fuel as a waste form, two fundamental sets of information are needed to define the waste form: (1) the radionuclide inventory and (2) the spent fuel characteristics including its release characteristics in a repository setting. The bulk of the radionuclide inventory is available or can be calculated. With regards to release characteristics, DOE assumed uranium metal fuel to provide an upper bound to the corrosion/dissolution for the entire range of fuel core materials (both metals and oxides) with congruent release of radionuclides (DOE 1999) as part of the Yucca Mountain repository license application submitted in 2008.

Waste Form Performance Modeling

Before solid radioactive waste may be placed in a subsurface disposal facility, a license must be obtained. Approval of the license is generally based on a performance assessment that determines the long-term impacts of the disposal facility on public health and environmental resources (for an example, see DOE 2008a). A sound scientific basis must be developed for determining long-term release rates of radionuclides from the radioactive waste forms for regulatory agencies and the public to accept the performance assessment. The long-term performance of solid radioactive waste is measured by the release rate of radionuclides into the environment, which in turn depends on corrosion or weathering rates of the solid waste form, solubility of the components in the resulting solution, and transport of the soluble components (and potentially colloids) in the subsurface. These rates strongly depend on the subsurface temperature and flow of moisture through the disposal facility as well as the reactive surface area of these solid materials. An effective performance assessment model is often some combination of a coupled thermo-hydro-mechanical-chemical model with coupled processes. The reactions involved depend on the characteristics of the solid matrix containing the radioactive waste, radionuclides of interest, and their interaction with surrounding geologic materials.

Corrosion and Erosion of Tanks, Process Vessels, and Containers/Packages

Radioactive wastes and nuclear materials must be safely stored, processed, and transported until permanent disposal. The physical, chemical, and radiological characteristics of the waste can make containment challenging precluding a one-size-fits-all approach. Alteration of either the nuclear materials or container materials under aging conditions, including interaction of the stored nuclear materials and container materials, must be characterized and managed to ensure the following:

- Containment is maintained to avoid inadvertent release and contamination;
- Nuclear materials in the storage system can be handled; and
- Nuclear materials remain in a form as when first placed in storage to ensure planned separations/waste form processing flow paths remain viable.

Attendant radiation from the nuclear materials can exacerbate challenges to the safe management system (e.g., radiolysis generating oxidizing species or radiation induced embrittlement).

High-Level Waste Tanks

The tanks at the Hanford and Savannah River Sites are approaching or have surpassed their expected service life. Several of the tanks at the Hanford Site are known or suspected of leaking radioactive waste into the soil. Given the current rate of retrievals, these tanks will need to remain in service for several more decades or alternatively new tanks will need to be constructed.

Currently, degradation mechanisms are managed through a rigorous corrosion control program that has been in place for the last three decades (Subramanian et al. 2008). This corrosion control program was developed from laboratory experiments and mitigates stress corrosion cracking, pitting, and general corrosion. The corrosion control program is verified by an in-service inspection for the tanks. Statistical methods have also been developed to understand the uncertainties associated with both the corrosion control program and the in-service inspection program (Hoffman et al. 2010). Additionally, as the waste is being retrieved, situations occur that are outside the present corrosion control program envelope for waste temperature and composition.

Process Piping and Vessels

Understanding the effect of erosion and corrosion in piping systems and vessels is of paramount concern, especially where conditions make it impossible to repair/replace components and/or the anticipated service life is long. Such conditions exist in the WTP black cells. Better understanding to predict corrosion plus nondestructive measurement techniques are needed to provide data for design and in situ monitoring. Currently, system monitoring does not provide the resolution necessary to adequately assess the anticipated degradation.

Spent Fuel Storage

The interim storage of production reactor and research reactor fuel of a multitude of designs is being performed at the Hanford Site, Savannah River Site, and Idaho National Laboratory. Both wet storage and dry storage systems have been implemented, and the storage practices with their technical bases are developed at the site level. Guidance for safe storage practices is drawn from the storage site experiences and lessons learned, and from the international community through International Atomic Energy Agency initiatives (IAEA 2012). Without end-state achievement through reprocessing or repository disposal, de facto extended storage will be in effect for the fuel in dry storage at the Hanford Site, in wet storage at the Savannah River Site, and in dry and wet storage at the Idaho Nuclear Technology and Engineering Center. A need exists to maintain the facilities and continue to store the fuel to minimize its degradation and enable availability of a full set of ultimate disposition options.

One example of a present interim storage configuration posing challenges to fuel alteration involves sectioned fuel pieces in water-filled cans, nested within a water-filled vented overpack canister at the Savannah River Site (Figure 10). The several galvanic couples in this configuration promote corrosion and, although the fuel can be handled and contained within this overpack canister, fuel alteration with time is unavoidable. To avoid restrictive fissile loading limits in some types of DOE spent nuclear fuel, nuclear criticality control measures, including an advanced neutron absorber coupled with standardized waste packages, were the baseline for disposal of DOE-managed spent nuclear fuel in the Yucca Mountain license application. The neutron absorber was an alloy of gadolinium in a nickel-chromium-molybdenum matrix. Gadolinium was chosen due to its high thermal neutron absorption cross section and low solubility in the anticipated repository environment. While DOE spent nuclear fuel is currently safely stored, extended surface storage periods of several hundred years would likely require repackaging. Ideally the spent fuel would have to be packaged only once before disposal. All disposal scenarios, including tuff (dense volcanic ash), granite, and salt, will likely require nuclear poisons for post-closure criticality controls under fuel reconfiguration scenarios. Therefore, nuclear criticality control measures remain the current reference configuration for disposal of DOE-managed spent nuclear fuel.

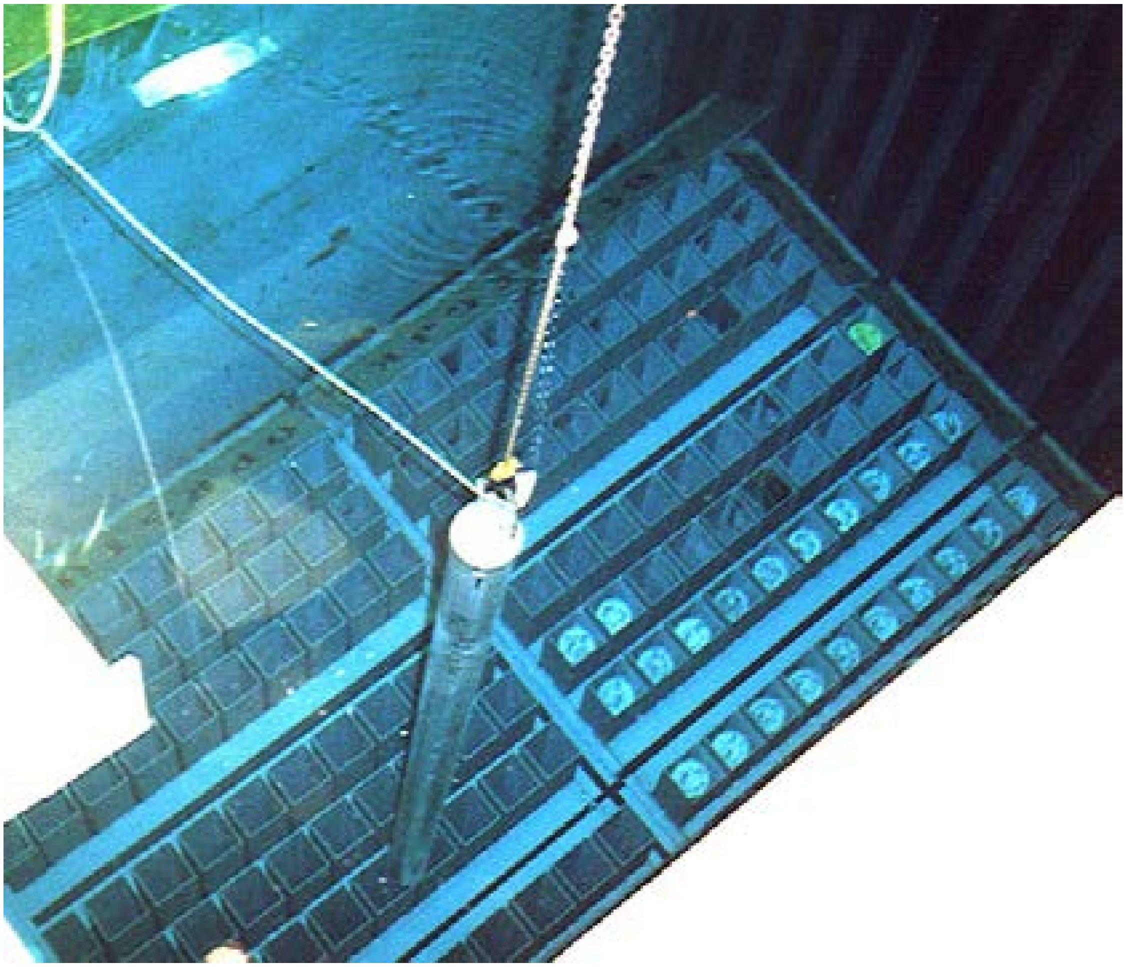


Figure 10. Storage Canister in the Savannah River Site L Basin (SRNL 2011). Image courtesy of Savannah River National Laboratory.

Waste Containers/Packages

Miscellaneous nuclear materials exist throughout the DOE complex that must be stored while waiting for a decision on an appropriate disposition path or packaged to facilitate disposition. These materials include accountable special nuclear materials, mixed waste streams (e.g., radioactive and hazardous constituents) that require remote/special handling, classified components, activated metals, sealed sources, radioisotope thermal generators, and other unique materials. These miscellaneous materials have been often referred to as “challenging materials” within EM.

The nature of the materials will often indicate the potential for storage issues. For example, materials containing appreciable concentrations of chlorides will increase the likelihood of storage container corrosion. Also, high-heat materials such as the cesium/strontium capsules at the Hanford Site are susceptible to swelling and/or phase changes as a result of changing storage conditions. Materials such as Hanford Site K-Basin sludge will change form if placed in dry storage with the potential to liberate gas.

The DOE-STD-3013 container is currently used for storage of excess weapons-usable plutonium at the Savannah River Site. A surveillance program is in place to validate that material stabilized and packaged to meet the 3013 standard could be safely stored for 50 years. Nondestructive and destructive evaluation on a representative sampling of the packages (determined statistically or using engineering judgement) is employed in the surveillance program. To date, no issues have been identified to preclude continued storage; however, pitting corrosion has been observed on the convenience can and the inner can (Figure 11) (Dunn and Louthan 2010). Observations of the pitting behavior have launched a new focus on determining whether such corrosion could credibly transition to stress corrosion cracking during storage and ultimately impact the long-term integrity of the 3013 container.

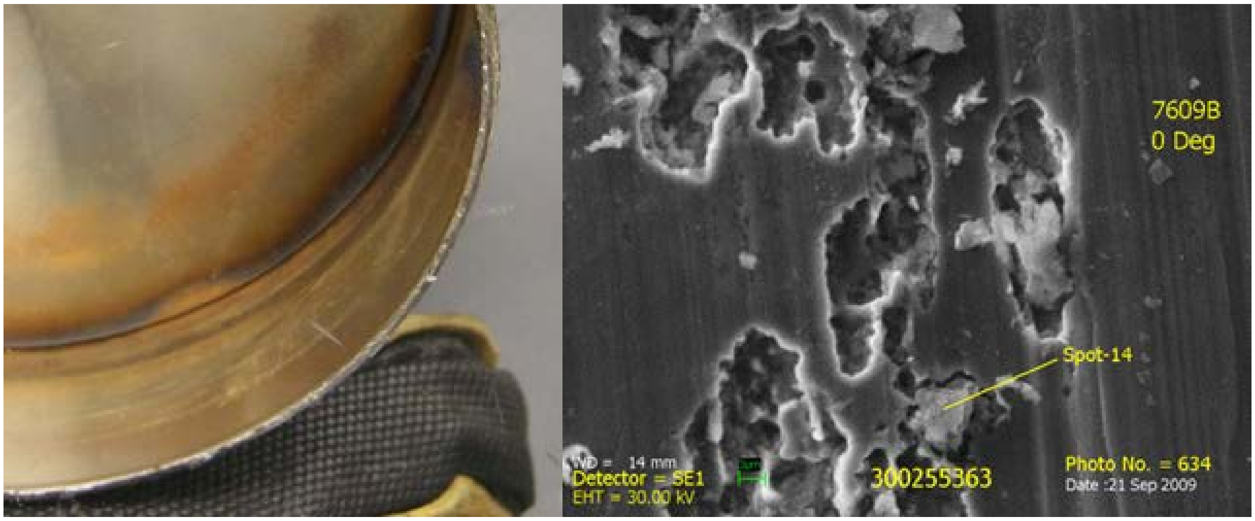


Figure 11. Inner Can Lid and Associated Pits (Dunn and Louthan 2010). Image courtesy of Savannah River Nuclear Solutions.

Radiation Damage and Radiolysis Impacts

The effects of radiation on both the wastes and waste forms are of particular importance. One major challenge is the identification and understanding of the mechanisms governing radioactive decay impacts on corrosion of materials in contact with aqueous systems (Bredt et al. 2008). A second challenge is the chemical and radiolytic hydrogen gas generation for TRU wastes. Understanding, preventing, and mitigating gas-generation-associated flammable gas buildup during storage, transportation, and disposal is a significant safety measure (Westbrook et al. 2015). A third challenge is the effects of radiation on the storage tanks and on the tank contents (Bredt et al. 2008).

Radiation Damage in High-Level Waste Glass

Weber (2014) provides an excellent review of the radiation effects on HLW glass and points to a number of ways that radiation effects glass performance. These include the following:

- Glass structure and solution composition could both be impacted by radioactivity;
- Beta-gamma radiation impacts on glass corrosion are primarily through radiolysis changing the composition of solution (Eh, pH, and dissolved species concentrations); and
- Radiation damage in glass waste forms are dominated by the ballistic effects of alpha particles and alpha nucleus recoil.

The rates of reaction will be most affected by the solution chemistry effects of radiolysis.

The impacts of beta-gamma radiation on glass corrosion are primarily through radiolysis changing the composition of solution (Eh, pH, and dissolved species concentrations) (Vienna et al. 2013). Physical properties of the glass are primarily controlled by ballistic effects of alpha recoil damage. These impacts can increase the stored energy of the glass, cause swelling or contraction of the glass by up to roughly 1 percent, and increase the glass fictive temperature. These effects are composition dependent and saturate at doses of roughly 10^{18} α-decay/g (somewhat independent of dose rate). Examples of these properties are shown in Figure 12. The mechanisms governing waste form dissolution will not change due to decay or radiation. The rates of reaction will be most affected by solution chemistry effects of radiolysis (Vienna et al. 2013).

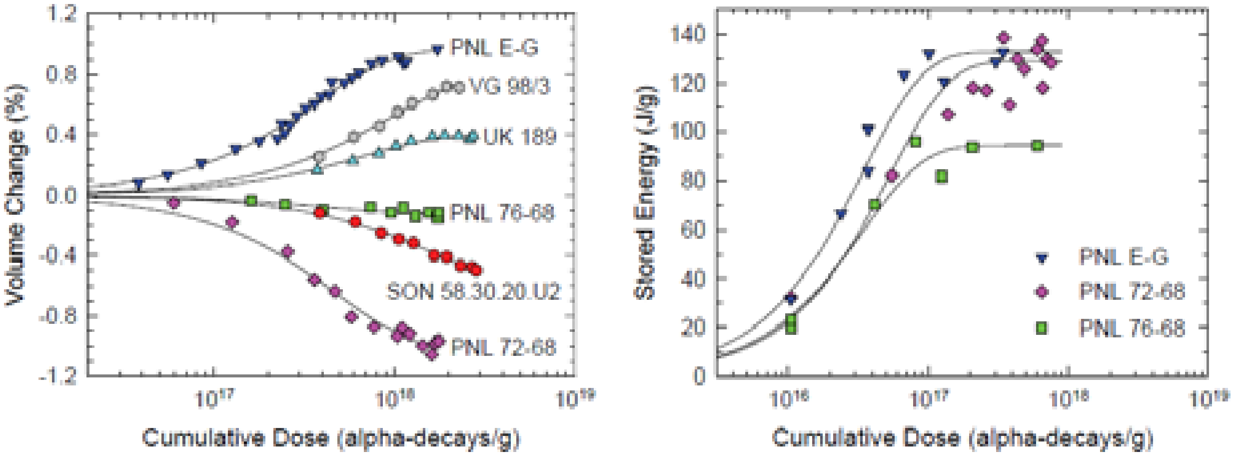


Figure 12. Impact of Cumulative Dose on Volume Change and Stored Energy. Reprinted from *Procedia Materials Science* (Weber 2014). Copyright 2014, with permission from Elsevier.

Radiolysis and Gas Formation

The waste tanks generally have active ventilation systems to prevent buildup of flammable vapor gases, such as hydrogen, which are produced by radiolysis of water. Radiolysis of solutions and dissolved organic compounds also produce volatile nitrogen-containing compounds that can impact corrosion of the tank headspace. Chemically derived volatile compounds can also be produced during the long storage periods of the waste. These compounds can impact corrosion of the tank headspace and present safety risks in tank farm operations. Examples of chemically derived volatile compounds include low-molecular-weight organics (e.g., trimethylamine), organomercury compounds (e.g., dimethlylmercury), and nitrogen compounds (e.g., ammonia and nitrous oxide). The formation and release of volatile organic compounds increases the burden on the ventilation system to maintain a nonflammable composition in the tank vapor space and reduce possible tank headspace corrosion. The organomercury compounds are highly toxic and thus represent an increased concern for exposure to onsite and offsite personnel.

Alpha-bearing wastes are uniquely challenging for storage due to the radiolysis reactions caused by the alpha-generating radionuclides in these wastes of widely varying composition. The alpha emitters can cause radiolysis of any water and/or organic materials present in the waste, potentially leading to hydrogen generation.

Combined Corrosion and Gas Generation

Understanding, preventing, and mitigating gas generation mechanisms and associated flammable gas buildup concerns during storage and transportation is a significant safety concern during storage, treatment, and transportation. One example is the generation of gases in the Hanford Site K-Basin sludges; another involves generation of hydrogen from spent aluminum-clad nuclear fuel assemblies during in-core operation and wet storage post irradiation.

Radiation-Resistant Materials for Waste Processing, Handling, and Monitoring

Many materials are exposed to elevated levels of radiation during waste handling, processing, and storage. For example, operations require equipment to move stored wastes including motorized vehicles and robotic devices. These devices require the use of materials, including electronics and sensors that are radiation resistant. In addition, radiation-resistant sensors are needed to monitor the storage facility.

Summary of Technological Challenges

- **Improved understanding of the mechanisms that affect melter operation.** The melter is a critical component in vitrification involving many chemical and physical processes that must be understood. For example, understanding technetium incorporation into or escape out of the glass melt during cold-cap melting would allow new approaches to be developed for technetium sequestration. Similarly, understanding sulfur trioxide solubility as a function of feed composition would allow for improved waste loading. In-melter analyses of these processes are also needed to provide this improved understanding. The ability to detect (and mitigate) spinel sludge within the melter would allow operation closer to crystal tolerance limits.
- **Enhanced loading of high-alumina wastes in glass.** This requires insight into the effects of composition and temperature history on the formation of nepheline and its associated impacts on the chemical durability of nuclear waste glasses.
- **Elucidation of the physical and chemical mechanisms responsible for degradation of waste forms.** This would catalyze the development of new waste forms able to stabilize radionuclides over long time scales. Specific needs include stabilization of highly mobile radionuclides (e.g., tritium, residual cesium, strontium) and long-lived isotopes (e.g., technetium, neptunium, iodine, and ^{14}C).
- **Improved models of long-term performance of waste forms**. The myriad chemical and physical factors involved in waste form performance makes the waste form stability particularly difficult to predict. For example, for some glass systems, an acceleration resulting in rapid alteration is observed after a period of low degradation rate. The ability to accurately predict if and when this behavior will occur is needed.
- **Robust methods for in-service characterization of tanks.** The tank environment is extremely challenging for reliable, long-term techniques for in-tank monitoring. In addition to the integrity of the tank walls and bottom, capabilities are needed for characterizing the liquids (e.g., pH and nitrate/nitrite), sludges, and gases (e.g., ammonia and hydrogen).
- **Development of new tank and storage materials and radiation-resistant materials for devices used to transport and monitor waste forms.** New materials are needed that can withstand the extremes (pH, corrosivity, reactivity, radiation, etc.) present in waste tanks, containers, pipes, and other systems. Radiation-resistant materials are also needed for devices used to transport and monitor waste materials within storage facilities.
- **Improved understanding of radiolysis processes.** This includes understanding the formation of gases and other chemical species (especially organometallics) via radiolysis under various conditions and the formation of aluminum compounds on the surface of aluminum-clad fuels.
- **Improved understanding of long-term corrosion processes in spent nuclear fuel.** In those situations where spent nuclear fuel is not processed and disposed of directly, a better understanding of

galvanic corrosion processes in the storage environments and their long-term effects on spent nuclear fuel behavior are needed. In addition, new materials are needed to develop transportation and disposal packages that mitigate nuclear criticality concerns.

- **New material systems for direct disposal of spent nuclear fuel.** Depending on regulations for a future repository, disposal scenarios, including tuff (dense volcanic ash), granite, and salt, may require neutron absorber materials (nuclear poisons) for post-closure criticality controls under fuel reconfiguration scenarios. Improved understanding of radionuclide release behavior from specific spent nuclear fuel would enable more informed repository performance assessment models to be developed.

CONTAMINANT FATE AND TRANSPORT IN GEOLOGICAL ENVIRONMENTS

Background

Remaining EM cleanup activities will involve remediation of groundwater, soil, and sediments in highly diverse environments that are contaminated with radionuclides, metals, and organic compounds, in some cases present as complex mixtures. Contamination resulted from instances of intentional disposal to the ground through injection wells, disposal pits, and settling ponds. A list of principal contaminants present across the DOE complex is provided in Table 1.

Table 1. List of Principal Contaminants Present at DOE Sites*

Radionuclides	Metals	Dense Nonaqueous Phase Liquid
Plutonium	Lead	Trichloroethylene
Strontium-90	Chromium(VI)	Dichloroethylene
Cesium-137	Mercury	Tetrachloroethylene
Uranium (various isotopes)	Zinc	Perchloroethylene
Tritium	Beryllium	Chloroform
Thorium	Arsenic	Dichloromethane
Technetium	Cadmium	Polychlorinated biphenyls
Radium	Copper	—
Iodine-129	—	—

* Hazen et al. 2008; Riley et al. 1992

Accidental spills and leaks from storage tanks and waste transfer lines also contributed to the contamination.

In some cases, little is known about the quantity of contaminants released, when they were released, or the composition of the release, presenting significant uncertainty about the location and long-term behavior of the contamination. Table 2 (NRC 2000) provides a brief synopsis of the geologic and climatologic variability that exists at the three larger sites. These serve as an example for the conditions present at various sites across the DOE complex. This broad range of climatic, ecologic, and geohydrologic conditions makes it difficult to predict future fate and transport. Without the benefit of new knowledge and technologies, this complexity makes site remediation and closure almost intractable.

Table 2. Geologic and Climatologic Variability at DOE Sites with Significant Subsurface Cleanup Needs

DOE Site	Climate	Geology and Hydrogeology	Surface Water Body	Approximate Depth to Groundwater
SRS	Humid, subtropical; average annual rainfall 122 cm (48 in)	Atlantic Coastal Plain with clay soils. The strata are deeply dissected by creeks, and most groundwater eventually seeps into and is diluted by creeks.	Savannah River	0 – 46 m (0 – 150 ft)
ORR	Humid, typical of the southern Appalachian region; average annual rainfall 138 cm (54.4 in)	Valley and ridge province bordering the Cumberland Plateau. Primary porosity is low but fracture porosity present. High clay content. Shallow water table.	Clinch River	6 – 37 m (20 – 121 ft)
HS	Arid, cool; mild winters and warm summers; average rainfall 16 cm (6.3 in)	Alluvial plain of bedded sediments with sands and gravels. Groundwater flows towards the Columbia River.	Columbia River	60 – 90 m (197 – 295 ft)

HS = Hanford Site; ORR = Oak Ridge Reservation; SRS = Savannah River Site

Current Approaches for Subsurface Remediation and Monitoring

Over the last two decades, the key research and technology gaps that impeded advances in subsurface cleanup have been identified in a variety of roadmaps, reviews, and other formal plans (DOE 1998, 2000, 2001, and 2008b; NRC 1996, 2000, NRC 2001, and 2009). These roadmaps, reviews, and plans were used to describe science and technology gaps and the work needed to fill those gaps. For example, the *Groundwater/Vadose Integration Program Roadmap* (DOE 1998) was created by the DOE Richland Operations Office to focus research activities, specifically projects sponsored under the EM Science Program, to address subsurface contamination issues at the Hanford Site. The document *A National Roadmap for Vadose Zone Science and Technology* (DOE 2001) was used to highlight the importance of understanding key processes that control the fate and transport of contaminants in the unsaturated zone. In addition, the National Research Council reviewed the EM program's intractable subsurface cleanup challenge again and identified the science and technology gaps that impeded subsurface cleanup at DOE sites (NRC 2000). These included the following:

- **Gap 1:** The behavior of contaminants in the subsurface is poorly understood.
- **Gap 2:** Site and contaminant source characteristics may limit the usefulness of EM baseline subsurface remediation technologies.
- **Gap 3:** Long-term performance of trench caps, liners, and reactive barriers cannot be assessed with current knowledge.

Finding solutions to the remaining subsurface problems will be the challenge facing DOE for the next several decades. To address the remaining first-of-a-kind challenges at the Hanford Site, Savannah River Site, and Oak Ridge Reservation—the larger and more complex sites, EM recognizes the need to place additional emphasis on implementing science-, engineering-, and technology-based solutions to reduce the technical risk and uncertainty in project execution (SEAB 2014). Many of the challenges that affect the larger sites also plague closure efforts at smaller sites (Idaho, Paducah, Portsmouth, West Valley, etc.). The following section provides a brief synopsis of the first-of-a-kind challenges that exist at the larger EM sites.

Characterization and Site Conceptual Models

Development and refinement of the conceptual site model (CSM) is key to achieving remedial action and monitoring objectives. Integrated systems-based characterization approaches are closely interrelated with the CSM. These are used to develop the CSM; continually test and refine the CSM throughout planning, design, and remedy implementation; and respond to changes in the CSM by making subsequent changes to the monitoring program.

Various Environmental Protection Agency guidance documents have been published that describe the CSM (for example, EPA 1996 and 2011). Aspects of CSMs include the following:

- The CSM provides the "ability to efficiently access and interpret data [which] is essential to guiding project teams through the entire cleanup process, from project planning to site completion. [The] creation and revision of a CSM [is] a primary project planning and management tool" (EPA 2011).
- The CSM includes both qualitative and quantitative descriptions of site-specific information, including the release and dispersal of the contaminant(s), relevant properties of the environment and how contaminant(s) interact with the environment, contaminant fate and transport processes, and potential routes of exposure and impacts of the contamination to plants, animals, and people. This information is designed to support subsequent analyses, evaluations, and decisions, including remedy selection and implementation and monitoring. The CSM documents current site conditions and is supported by maps, cross sections, and site diagrams (EPA 1996).
- The CSM is a "living" framework that continually evolves as data are collected and synthesized and as the focus of the CSM, monitoring objectives, and key decisions change throughout characterization and remediation. The Environmental Protection Agency describes this as the CSM lifecycle (EPA 2011).

The major elements that make up an integrated CSM are the waste release conditions, boundary conditions, hydrogeologic setting, geochemical/microbiological setting, exposure pathways, and point(s) of compliance. Each of these is important to contaminant movement in the subsurface and is interrelated.

Waste was released at DOE sites under extremely varied conditions. For example, waste leaked from Hanford Site HLW tanks was highly alkaline, while waste released to some Savannah River Site seepage basins was highly acidic. The chemical nature of the released waste is often the driving force for geochemical and microbiological reaction networks that affect contaminant behavior. The volume and frequency of release of waste from the source varied significantly as well, from single isolated spills to 108 liters per year for decades in some seepage basins. Contamination originating from small spills, slow leaks, and solid waste trenches requires infiltrating water to move it through the vadose zone into the saturated zone. In contrast, the massive volumes of liquid waste disposed in cribs and seepage basins provided the water to, in some cases, move contamination into the saturated zone; in other cases, the waste influenced the direction of local groundwater flow by causing mounds in the water table; and in other, cases the waste remains within the deep vadose zone.

Boundary conditions are the features and processes that control mass balance of water in a subsurface system, maintaining a driving force that moves groundwater. These conditions also vary substantially across the DOE complex, most dramatically between sites with high and low yearly precipitation. At sites with high amounts of precipitation, local streams generally control the movement of contamination plumes in groundwater, sometimes providing recharge water, but more often receiving discharge of contamination plumes. At sites with low precipitation, local streams are less important and evapotranspiration may be an important influence on groundwater flow and contaminant movement.

Boundary conditions also vary with time, often seasonally, but in special cases with high frequency, as is the case with the Columbia River level at the Hanford Site.

Hydrogeologic settings influence the rate and direction of groundwater flow as well as the dispersion a contamination plume undergoes as it migrates. Porous flow systems consist of clay, sand, gravel, and cobbles, usually deposited by sedimentary processes that include water and airborne deposition. The particles form a network of pores through which subsurface water can move. Understanding flow in these systems is complicated by the heterogeneity in grain size and degree of cementation introduced by the geologic process responsible for their deposition and diagenesis. Fracture systems can occur in sedimentary, metamorphic, or igneous rocks. The fractures are formed by stresses within the earth and can have regular patterns. Nevertheless, prediction of groundwater flow in fractured systems is difficult and at some sites, such as the Oak Ridge Reservation, karstic terrains are important. These form by dissolution of limestones, creating large pathways for groundwater flow in which contaminants can move very rapidly.

Geochemical and microbiological reaction networks are the reactive controls on contaminant mobility. These include reactions that involve contaminants, reactions of the bulk chemistry of the released waste with aquifer minerals, and microbial reactions stimulated by the bulk chemistry of the waste. Major contaminant reactions include aqueous complexation, surface complexation, intraparticle diffusion, sorption to mineral surfaces, ion exchange, precipitation, and changes in valence state for certain contaminants. These are interrelated and influenced by the bulk chemistry of the groundwater-sediment-waste system. Thus, reaction networks must include reactions that change pH, redox potential, concentrations of complexing ligands, nature of mineral surfaces, and amount and nature of natural organic matter. Microbes also play an important role in the mobility of many contaminants, most notably by directly catalyzing changes in certain contaminant’s valence state or changing the bulk chemistry of the groundwater, causing oxidation or reduction of redox-sensitive contaminants. Microbes can also produce mineral phases that react with contaminants (e.g., biogenic magnetite or pyrite) and can be sorption sites for contaminants.

Characterization is the process of collecting information at a contaminated site on the elements of the CSM. The qualitative and quantitative data collected are integrated into development of the CSM. Characterization often continues into the remedial phase of a waste site, with the CSM continually updated as new characterization data warrants. The initial phase of characterization is initially to understand the nature and extent of contamination. More detailed investigation of the CSM elements can be done in parallel, but has often been done subsequently. One of the important lessons learned during decades of soil and groundwater cleanup activities is that it is far more efficient and cost effective to approach initial characterization with the perspective of the waste site as an integrated system. There are tools and support to facilitate this approach to site characterization (e.g., http://www.triadcentral.org/). Data collection tools for characterization are often the same as those used for site monitoring, although the objectives of the data collection are different.

The understanding of the nature of waste release is best at sites where historical information on the nature of the waste and disposal history exists. In the absence of this information, the nature of the waste can be inferred from the groundwater chemistry and measurements on subsurface materials obtained near the waste source. The amount and flux of waste release can be reconstructed from plume size, seepage rates, etc. Inverse modeling is also useful for reconstructing waste release.

Boundary conditions are generally relatively easy to characterize. Existing knowledge of regional hydrology and climate conditions facilitates boundary condition characterization. Stream levels and flow are easily measured and US Geological Survey data often exists for larger streams and rivers. Likewise, water levels at the site are easily measured in available wells and piezometers. Geophysical tools can also be used to measure water levels on a larger scale. There are remote imaging databases that provide evapotranspiration data for many parts of the country.

Hydrogeologic settings are mostly characterized by coring boreholes. Core samples and downhole geophysical tools have been used to correlate geologic strata across a waste site and obtain hydrogeologic properties such as porosity and water saturation. Direct push technology can be used in sediments that are poorly consolidated and lack large cobbles to determine stratigraphic relations and other physical properties of the sediments. Surface geophysical tools, such as various forms of seismic surveys and surface resistivity surveys, can be used to delineate interfaces between subsurface materials with differing properties (e.g., interfaces between different rock types). Permeability measurements can be made on cored samples, in individual wells by slug tests, by multiwell pump tests, and by multiwell monitoring of injected tracers.

Reaction networks are determined by a combination of field and laboratory measurements and studies. Spatial and temporal differences in bulk water chemistry and microbial communities determined from field measurements can indicate types and rates of reactions. More accurate chemical and microbial reaction rates are determined by laboratory studies of field samples or simulants of field samples. Currently, properties of subsurface materials (e.g., mineralogy, specific surface area, zero point of charge) must be determined in the laboratory. In addition, ever-increasing sophistication in spectroscopic and microscopic techniques allows greater understanding of the nature of adsorption, precipitation, and coprecipitation.

Sustainable Remediation

As is widely acknowledged, EM sites present some of the greatest challenges within the field of environmental remediation. Implementing sustainable remediation strategies at these sites will require an understanding of the soil structure, hydrologic, and biogeochemical conditions that affect contaminant mobility over long periods, technical options for remediation and/or containment of these contaminants, and an understanding of the longevity of containment options. Some of the remedial technologies currently being considered to mitigate contaminant release from source zones are contaminant mass reduction, contaminant stabilization, and hydraulic control through the use of physical barriers, immobilizing or transforming contaminants, and mobilizing and/or extracting contaminants. Table 3 provides a list of technologies that have been tested and/or used at the Savannah River Site, Oak Ridge Reservation, and Hanford Site.

Table 3. Remedial Technologies Tested/Used at DOE Sites

Category	Cleanup Approach/ Technology	Sites Implementing Technology
Contaminant mass reduction	Excavation	SRS, ORR, HS
	Groundwater pump and treat	SRS, ORR, HS
	Soil vapor extraction	SRS, HS
	Passive (baroballs and solar powered microblowers)	SRS
	Chemical oxidation	SRS
	Recirculation wells	SRS
	Thermal treatment (steam injection, bulk vitrification, and electrical resistance heating)	SRS, ORR
	Bioremediation	SRS, ORR, HS
	Phytoremediation (enhanced evapotransporation)	SRS
Contaminant stabilization	Monitored natural attenuation	SRS, ORR, HS
	Subsurface barriers	SRS, ORR, HS
	In-situ stabilization (chemical and biological)	SRS, ORR, HS
Hydraulic control	Surface barriers (caps)	SRS, ORR, HS
	Permeability control (grouting)	ORR, HS
	Desiccation	HS
	Pore-water extraction	HS

HS = Hanford Site; ORR = Oak Ridge Reservation; SRS = Savannah River Site.

Physical barriers (e.g., vertical barriers, surface caps, or horizontal barriers) are used to manage contaminated sites by either isolating the source zone contamination, controlling water infiltration, or minimizing downward migration of contaminants. Physical, chemical, and/or biologically mediated processes (e.g., permeable reactive barriers, redox barriers, or bioremediation) are also used to minimize mass flux from a source by immobilizing or transforming contaminants into a more resistant form. Additional remedial techniques also exist that mobilize and extract contaminants (e.g., soil washing, soil flushing, and phytoremediation) from groundwater and soil to control source-term release. Although the basis for these remedial technologies is the application of source-term control techniques that reduce mass flux to meet cleanup objectives, designing sustainable strategies is extremely difficult. Furthermore, predicting their performance over the necessary intervals of long-term stewardship (i.e., hundreds to thousands of years) is equally difficult. For additional details on the technologies listed beyond the discussion provided above, see NRC (1999) and the references contained therein. For additional discussion on technologies that can be applied to remediate deep vadose zone metals and radionuclides, see Dresel et al. (2008).

The major factors that make the design of sustainable strategies challenging are associated with the need for an improved understanding of how key physical properties and coupled hydrodynamic and biogeochemical processes will influence implementation. These factors are exacerbated by the heterogeneity of the subsurface environment. Another key aspect is the need for a systems-based approach to address the various portions of a contaminant plume (primary and distal) during a remedial action. Implementing a systems approach will require use of an attenuation-based remedy scheme, either as an individual remedial action or with an in situ remedial technology. Attenuation-based remedies use natural processes, such as biogeochemical gradients, to minimize or eliminate contaminant migration. Furthermore, a process for transitioning from active remediation to attenuation-based approaches at sites is also needed to develop sustainable remediation strategies.

Effect of Physical Properties on Implementation of Remedial Strategies

The key physical properties that typically affect the successful implementation of remedial techniques are associated with subsurface heterogeneity and the interrelated challenge of spatial and temporal scale up. Heterogeneity can have a significant influence on the configuration and distribution of contaminants. For example, centimeter-scale silt lenses have been shown to exert a major influence on fluid flow and contaminant migration in the subsurface at the Hanford Site (Zachara et al. 2004). Additionally, spatial differences in permeability can result in ineffective treatment of subsurface contamination with a reagent-based treatment technology. In other words, the presence of preferential flow paths in the subsurface environment can cause a reagent-based treatment technology to treat the more permeable zones and miss the less permeable ones. In general, the less permeable zones often contain a large portion of the source contamination and have a significant effect on the long-term ability to remediate the dilute fringe of plumes. Several of the innovative technologies mentioned above have been successfully tested and behave in a predictable manner at the laboratory and intermediate scale, but because of the changes in physical properties that occur with changes in scale, operating these technologies at the field scale can result in diminished efficiency and predictability.

As a result, controlled laboratory-scale batch studies are deficient in predicting phenomena observed at the field scale because fluids in subsurface environments are not well mixed. Intermediate-scale investigations are also limited because they do not provide an understanding of the core structure and mechanisms that control macroscopic observations. This refers to the lack of direct information on the local, diffusion-limited processes that occur as a result of variations in subsurface permeability, preferential flow paths, and sediment structure. Therefore, to address the issues associated with heterogeneity and scale, controlled vadose zone field experiments of remedial technologies are needed to bridge the gap between laboratory- and intermediate-scale mechanistic and implementation studies and field-scale application.

Effect of Hydrodynamic and Biogeochemical Conditions on Remedial Performance

The manner in which physical, chemical, and microbial processes upscale from the pore level to soil profiles, watersheds, and groundwater basins is currently limited by a lack of direct measurements of diffusion-controlled processes. Additionally, hydrodynamic and biogeochemical subsurface conditions can affect the pre- and post-remedial implementation phases. Biogeochemical conditions are important because they can (1) slow or prevent the movement of contaminant- or reagent-based treatment technology, (2) decrease the reactivity of a treatment technology, (3) reverse an existing in situ stabilization scheme (e.g., reoxidation of uranium immobilized by a permeable barrier), and (4) be perturbed to manipulate existing conditions to enhance a remedial approach. Therefore, new research must be conducted at scales of the coupled chemical, biological, and physical processes to determine their impact on implementing remedial strategies.

Long-Term Effectiveness of Natural or Enhanced Attenuation

The use of natural attenuation processes, either alone or enhanced, to reduce or eliminate contaminant migration in groundwater has become more popular within the past decade. Attenuation-based remedies include in situ processes such as biodegradation, dispersion, dilution, sorption, volatilization, radioactive decay, and chemical or biological stabilization, transformation, or destruction of contaminants. For example, attenuation-based remedies for mercury include the addition of stannous chloride to remediate surface water, immobilization with hydrogel encapsulation, or adsorption by mesoporous silica (Self-Assembled Monolayers on Ordered Mesoporous Supports, SAMMS™). Techniques such as these can be used with attenuation-based remedies to place contaminated sites on a path to long-term stewardship. To approve attenuation-based remedies, regulators and stakeholders will require defensible technical data that provide a scientific foundation for attenuation-based remedies.

Systems-Based Monitoring

Each phase of environmental monitoring in support of cleanup activities has distinct objectives. Monitoring activities before and during remediation activities or stabilization of a contaminated site are defined here as process monitoring. Following remediation, monitoring that assesses the effectiveness and short- to mid-term stability of remediation objectives is called performance monitoring. Finally, long-term monitoring is defined as those activities used to confirm and assess stability and maintenance of a site in closure. Over the last decade it has become clear that site closure is not always clearly defined, particularly if there are residual wastes. Closure at many sites means that the remedy has been implemented but the site will need to be monitored to ensure the remedy is sustaining.

DOE conducts monitoring in a range of environmental media, including surface water, groundwater, soils, sediment, air, flora, and fauna. This approach currently requires expensive sampling of monitoring networks, ranging in size from tens to hundreds of sampling locations, and resulting in costs of hundreds of thousands to millions of dollars per year for sampling and data management (Reed et al. 2000). In addition, long-lived contaminants will be present for many decades or even centuries at approximately 100 sites, posing long-term monitoring challenges and opportunities. As a consequence of the resources required to maintain a monitoring program for a long period, most monitoring optimization efforts have focused on long-term monitoring (DOE 2011). Thus, there is a critical need to advance monitoring approaches that move away from the cost and labor intensive point-source monitoring to more leading edge, systems-based monitoring strategies that use early indicator parameters and flux-based understanding.

Previous DOE efforts to improve monitoring have focused on the state of available technologies (DOE 2011) and/or optimization of long-term monitoring locations, analytes, and sample frequencies. Efforts have been interdepartmental and cross-disciplinary (DOE 2009). In 2012, EM published the keystone document for DOE's plan on monitoring, *Scientific Opportunities for Monitoring at Environmental Remediation Sites* (Bunn et al. 2012). This document provides the scientific and technical foundation to advance monitoring approaches beyond traditional sampling approaches. It presents a cross-disciplinary perspective of opportunities and challenges for systems-based monitoring in multiple media including the background and context for monitoring at DOE sites.

DOE's vision for advancing monitoring through an integrated systems-based approach identifies in detail the scientific and technical opportunities associated with monitoring at DOE sites. Specifically, challenges and opportunities associated with monitoring focus on (1) reliance on CSMs and evolution of CSMs throughout the monitoring phases; (2) in addition to point measurements, the use of flux-based measurements where possible; (3) together with conventional data, the use of innovative monitoring tools including surrogates, early indicator parameters, bioassessments, geophysics/remote sensing, predictive analyses/models, and information management to collect multiple lines of evidence; and (4) methods to integrate monitoring information to understand the system as a whole, update the CSM, and reduce monitoring costs, risk, and schedule.

Geophysical Assessment Tools

The overall objective of geophysical assessment tools in monitoring is to indicate changes, compared to a baseline survey, in spatial subsurface information caused by a remedial process, post-remedial effects, or long-term changes in plume stability. Geophysical measurements for monitoring can be collected using airborne, surface, and/or downhole tools and techniques. Geophysical assessment tools can be used in a systems-based approach to process, performance, and long-term monitoring. The operational difference between the use of geophysical tools for characterization and monitoring is the frequency of data collection and the duration. Geophysical surveys are typically done only once during characterization. Process monitoring requires high-frequency data collection over a relatively short duration; the actual frequency depending on the process. Long-term monitoring requires low-frequency data collection over long timeframes. Performance monitoring lies between these two. This can be a factor in the choice of geophysical tools. Ideally, tools that use simple robust sensors could be used for long-term monitoring because a network could be deployed and left in place for decades and personnel could conduct a survey every few years. For process monitoring, more automated systems that collect data on a frequency of days to months would be ideal, but the system can be less robust.

Bioassessment Tools

Changes in the composition and function of a biological community (e.g., in response to remediation) can be identified and tracked to better understand, predict, and assess the efficacy of remediation strategies. Microorganisms, invertebrates, vertebrates, and plants almost never exist as individual species in nature, but as integrated communities. Changes to their environmental conditions impact these communities and vice versa. For example, characterization of baseline biological conditions within an environment (diversity or probable metabolic potential) can be used to establish the state of the community, and process, performance, and long-term monitoring can assess the changes or recovery of the community throughout the remediation lifecycle. Microbes may be used for soil and groundwater remediation (e.g., bioaugmentation, biostimulation, monitored natural attenuation). Invertebrates, vertebrates, and plants can take up or sequester specific contaminants (e.g., phytoremediation) or serve as indicators of contaminant flux as well as toxicity testing.

Surrogates and Indicators

Surrogate parameters are easily measured or monitored and are used for more difficult-to-measure analytes or a suite of analytes or parameters to distinguish a change in baseline conditions and indicate that additional investigation is necessary (Gilmore et al. 2006). The concept of surrogates is based on use of indicator parameters to imply the behavior of regulated analytes. The surrogate approach calls for development of a sentinel parameter that can provide time-sensitive data regarding a change in site conditions. Surrogate and indicator monitoring are appropriate for a wide variety of media, including surface conditions (soil, vegetation, and hazardous wastes), surface water, groundwater, air, and fauna. Surrogate and indicator methods may be based on one of more of the following:

- Simple, low-cost, field-based measurements rather than comprehensive analytical laboratory measurements (e.g., master variables such as conductivity, pH, oxidation reduction potential, dissolved oxygen, moisture content, and barometric pressure).
- Remote sensing, such as surface or airborne geophysical methods, allows capture of data from a large area or volume in a single event or limited laboratory analysis.

Surrogate parameters are best suited to long-term monitoring where earlier characterization or monitoring has provided the technical basis for the validity of the surrogate. During long-term monitoring there is sufficient time to react when a surrogate parameter triggers concern that the plume may be unstable or conditions are changing in a way that will mobilize stabilized contaminants. This may not be true for process and performance monitoring.

Predictive Analysis Tools

Predictive analyses integrate scientific data and monitoring results from environmental systems into a common framework to inform the development of monitoring networks and strategies. Predictive analyses can range from parametric analyses (e.g., statistical evaluation of monitoring data) to detailed analytical and numerical models. Predictive analyses can be used for the following purposes:

- Choosing locations for sampling points or sensor placement as well as frequency of data collection for process, performance, and long-term monitoring;
- Estimating necessary duration of process, performance, and long-term monitoring for planning purposes; and
- Determining optimum surrogate parameters for long-term monitoring.

Information Management Tools

Information management is central to the task of designing and implementing effective monitoring programs and long-term environmental care at DOE sites. The goal of information management at environmental remediation sites is not only to collect, organize, analyze, and archive data, but also to synthesize data into meaningful information that can be easily recognized and communicated. Another key goal of information management is to engage and inform both site-specific and national stakeholders. Over the long term, environmental monitoring data at each site needs to be synthesized to determine the protectiveness and performance of the environmental remedy and confirm that site conditions do not pose a threat to human health or ecological receptors. The challenge is achieving this in the most efficient way given the enormous quantities and varied types of data generated by process, performance, and long-term monitoring.

Predictive Modeling

Both field experience and emerging science provide evidence that complex hydrogeology and reactive transport are important in developing accurate conceptual and numerical models for key contaminants in heterogeneous settings. This is not to say that complex conceptual and numerical models are required for all DOE problems; it is important to match models to site needs and conditions. This is done by developing conceptual models that describe site conditions and process controls on contaminant fate and transport. After the conceptual model is formulated, an evaluation process is followed to determine if numerical modeling is needed. Numerical modeling may not be necessary for sites with simple plumes that are stable or shrinking. In these cases, numerical modeling may not provide the needed benefit in terms of uncertainty reduction, remediation design, or monitoring optimization. However, for complex soil and groundwater contamination problems at the remaining EM cleanup sites, numerical models may be needed for integrating data and understanding coupled hydrologic, geochemical, and microbiological processes as well as predicting the impact of actions and treatments over stewardship timeframes and relevant field scales.

These models are used to (1) integrate, test, and refine multiscale conceptual models that incorporate hydrogeologic and biogeochemical properties and processes at varying scales, and (2) guide selection, implementation, and optimization of remedial treatments. Examples of these models include biogeochemical and metabolic models that integrate and describe microbiologic effects as well as reactive transport forward and inverse models to forecast plume migration. Also included is the need to assess active remediation and the effectiveness of natural attenuation as well as engineering models for optimization and uncertainty analyses.

Summary of Technological Challenges

- **Systems-level approaches for effective treatment strategies.** Strategies must include delivery of materials for treatment or containment that take into account variations in physical and hydrologic environments (e.g., deep vadose zone) and the complex and poorly understood relationship between baseline biological, chemical, hydrologic, and geologic effects. Emphasis needs to be placed on strategies that can treat multiple contaminants (radionuclides and hazardous) simultaneously. This approach will require development of new chemical and physical processes for remediation as well as optimization of natural biogeochemical processes. For example, new approaches may be designed that rely on reagents for near-term remediation and transition in the longer term to natural attenuation.
- **New methods for monitoring, measuring, and verifying the design and long-term effectiveness of a remediation process**. These methods, based both on point-source and flux-based measurements, would assist in designing remediation approaches and evaluating the long-term efficiency of primary plume treatment strategies. Innovative capabilities are needed to monitor surrogates, early indicator parameters, bioassessments, and geophysics/remote sensing to allow these multidimensional data to be incorporated into predictive models of remediation effectiveness. This integrated approach to understand the system as a whole will produce a more accurate CSM and reduce monitoring costs, risks, and schedule.
- **Improved data analytics**. New capabilities are needed to incorporate and correlate disparate sets of data that span broad spatial and temporal regimes into CSMs. Another complication is that subsurface heterogeneity, ranging from molecular to regional, impedes the understanding of contaminant transport that is critical to the formulation of remediation strategies. Further, most laboratory studies are done on time scales of hours to months, whereas many environmental processes occur over years to decades. Work has been done on "aging" effects on adsorbed or precipitated contaminants, but the work is not sufficiently robust to incorporate into CSMs.
- **Improve predictive models of site evaluation and treatment at all scales.** Current models do not address critical parameters that are required to describe the coupled physicochemical phenomena (oxidation and reduction, adsorption and precipitation, and mass transfer) that span multiple scales and control contaminant migration in heterogeneous subsurface systems. Systems-based conceptual models are needed that capture and accurately represent the appropriate level of subsurface complexity to predict plume evolution. These models must include considerations of surface water and groundwater interface interactions, geological structure, chemical reactivity, multiphase transport, and many other factors.

REFERENCES

Blankenship JK, CA Langton, JC Musall, and WB Griffin. 2012. New Materials Developed To Meet Regulatory and Technical Requirements Associated with In-situ Decommissioning of Nuclear Reactors and Associated Facilities. SDD-2012-00003, Savannah River Nuclear Solutions, Aiken, South Carolina.

Bonnesen PV, LH Delmau, BA Moyer, and RA Leonard. 2000. "A Robust Alkaline-Side CSEX Solvent Suitable for Removing Cesium from Savannah River High Level Waste." *Solvent Extraction and Ion Exchange* 18: 1079–1107.

Bonnesen PV, LH Delmau, BA Moyer, and GJ Lumetta. 2003. "Development of Effective Solvent Modifiers for the Solvent Extraction of Cesium from Alkaline High-Level Tank Waste." *Solvent Extraction and Ion Exchange* 21: 141–170.

Bray LA, KJ Carson, and RJ Elovich. 1993. *Initial Evaluation of Sandia National Laboratory-Prepared Crystalline Silico-Titanates for Cesium Recovery*. PNL-8847, Pacific Northwest Laboratory, Richland, Washington.

Bray LA, JE Amonette, GN Brown, TM Kafka, and SF Yates. 1995. *Efficient Separations and Processing Crosscutting Program: Develop and Test Sorbents*. PNL-10750, Pacific Northwest Laboratory, Richland, Washington.

Bredt P, AR Felmy, PA Gauglitz, D Hobbs, S Krahn, N Machara, M McIlwain, BA Moyer, AP Poloski, K Subramanian, JD Vienna, and B Wilmarth. 2008. *Scientific Opportunities to Reduce Risk in Nuclear Process Science*. PNNL-17699, Pacific Northwest National Laboratory, Richland, Washington.

Brown GN, LA Bray, CD Carlson, KJ Carson, JR DesChane, RJ Elovich, FV Hoopes, DE Kurath, LL Nenninger, and PK Tanaka. 1996. *Comparison of Organic and Inorganic Ion Exchangers for Removal of Cesium and Strontium from Simulated and Actual Hanford 241-AW-101 DSSF Tank Waste*. PNL-10920, Pacific Northwest Laboratory, Richland, Washington.

Brown SJ. 2010. "Caustic Side Solvent Extraction At the Savannah River Site: Operating Experience and Lessons Learned – 10105." In *WM2010 Conference Proceedings*, March 7–11, 2010, Phoenix, Arizona.

Bunn AL, DM Wellman, RA Deeb, EL Hawley, MJ Truex, M Peterson, MD Freshley, EM Pierce, J McCord, MH Young, TJ Gilmore, R Miller, AL Miracle, D Kaback, C Eddy-Dilek, J Rossabi, MH Lee, RP Bush, P Beam, GM Chamberlain, J Marble, L Whitehurst, KD Gerdes, and Y Collazo. 2012. *Scientific Opportunities for Monitoring at Environmental Remediation Sites (SOMERS): Integrated Systems-Based Approaches to Monitoring*. DOE/PNNL-21379. Pacific Northwest National Laboratory, Richland, Washington.

Daniel RC, JM Billing, RL Russell, RW Shimskey, HD Smith, and RA Peterson. 2011. "Integrated Pore Blockage-Cake Filtration Model for Crossflow Filtration." *Chemical Engineering Research and Design* 89(7): 1094–1103.

Dimenna RA, HH Elder, JR Fowler, RC Fowler, MV Gregory, T Hang, RA Jacobs, PK Paul, JA Pike, PL Rutland, FG Smith III, SG Subosits, GA Taylor, SG Campbell, and FA Washburn. 2001. *Bases, Assumptions, and Results of the Flowsheet Calculations for the Decision Phase Salt Disposition Alternatives*. WSRC-RP-99-00006, Rev. 3, Washington Savannah River Company, Aiken, South Carolina.

DOE – US Department of Energy. 1996. *Waste Acceptance Product Specifications for Vitrified High-Level Waste Forms (WAPS)*. DOE/EM-0093, US Department of Energy, Washington, DC.

DOE – US Department of Energy. 1997. L*inking Legacies: Connecting the Cold War Nuclear Weapons Production Processes to their Environmental Consequences*.US Department of Energy, Washington, DC.

DOE – US Department of Energy. 1998. *Groundwater/Vadose Zone Integration Project Science and Technology Summary Description*. DOE/RL-98-48, Vol. 3, Rev. 0, DOE/Richland Operations, Richland, Washington.

DOE – US Department of Energy. 1999. *DOE Spent Nuclear Fuel Information in Support of TSPA-SR*. DOE/SNF/REP-047, Rev. 2, DOE/Idaho Operations Office, Idaho Falls, Idaho. TIC: 252089.

DOE – US Department of Energy. 2001. *A National Roadmap for Vadose Zone Science & Technology: Understanding, Monitoring, and Predicting Contaminant Fate and Transport in the Unsaturated Zone*. DOE/ID-10871, Rev. 0, DOE/Idaho Operations Office, Idaho Falls, Idaho.

DOE – US Department of Energy. 2002. *Groundwater/Vadose Zone Integration Project Science and Technology Summary Description*. DOE/RL-98-48, Vol.3, Rev. 1, DOE/Richland Operations, Richland, Washington.

DOE – US Department of Energy. 2008a. Letter to NRC: "Yucca Mountain Repository License Application (LA) for Construction Authorization." WM-00011, June 3, 2008, Washington, DC.

DOE – US Department of Energy. 2008b. *Engineering & Technology Roadmap: Reducing Technical Risk and Uncertainty in the EM Program*. Office of Environmental Management, Washington, DC.

DOE – US Department of Energy. 2009. *DOE-EM Long-Term Monitoring Technical Forum Summary Report*. SRNL-RP-2009-00845, Savannah River National Laboratory, Aiken, South Carolina; US Department of Energy Office of Environmental Management, Washington, DC, http://sti.srs.gov/fulltext/SRNL-RP-2009-00845.pdf.

DOE – US Department of Energy. 2011. *EM Office Develops Technology to Revolutionize Subsurface Exploration*. Vol. 3, Issue 16. US Department of Energy, Office of Environmental Management, Washington, DC.

DOE – US Department of Energy. 2015a. "Soil & Groundwater Remediation." http://energy.gov/em/services/site-facility-restoration/soil-groundwater-remediation.

DOE – US Department of Energy. 2015b. "EM Safely and Efficiently Manages Spent Nuclear Fuel." http://energy.gov/em/em-safely-and-efficiently-manages-spent-nuclear-fuel.

DOE – US Department of Energy. 2015c. *Departmental Response: SEAB Task Force Recommendations on Technology Development for Environmental Management*. US Department of Energy, Washington, DC. http://energy.gov/seab/downloads/report-task-force-technology-development-environmental-management

Dosch RG. 1978. *The Use of Titanates in Decontamination of Defense Wastes*. SAND-78-0710, Sandia Laboratories, Albuquerque, New Mexico.

Dresel PE, MJ Truex, and K Cantrell. 2008. *Remediation of Deep Vadose Zone Radionuclide and Metal Contamination: Status and Issues*. PNNL-18114, Pacific Northwest National Laboratory, Richland, Washington.

Dunn K and M Louthan. 2010. "Evidence of Corrosive Gas Formed by Radiolysis of Chloride Salts in Plutonium-Bearing Materials." *Journal of Nuclear Materials Management* 38(3): 82.

Edwards TB, KG Brown, and RL Postles. 2006. *SME Acceptability Determination for DWPF Process Control (U)*. WSRC-TR-95-00364, Rev. 5, Savannah River National Laboratory, Aiken, South Carolina.

EPA – US Environmental Protection Agency. 1996. *Soil Screening Guidance: User's Guide*. EPA 540-R-96-018, US Environmental Protection Agency, Washington, DC, www.epa.gov/superfund/resources/soil/ssg496.pdf.

EPA – US Environmental Protection Agency. 2011. Environmental Cleanup Best Management Practices: Effective Use of the Project Life Cycle Conceptual Site Model. Quick Reference Fact Sheet. EPA 542-F-11-011, Office of Solid Waste and Emergency Response, Office of Superfund Remediation and Technology Innovation, US Environmental Protection Agency, Washington, DC, http://www.epa.gov/tio/download/remed/csm-life-cycle-fact-sheet-final.pdf.

Fiskum SK, ST Arm, MS Fountain, MJ Steele, and DL Blanchard, Jr. 2006a. Spherical Resorcinol-Formaldehyde Resin Testing for ^{137}Cs Removal from Simulated and Actual Hanford Waste Tank 241-AP-101 Diluted Feed (Envelope A) Using Small Column Ion Exchange. PNWD-3697, Battelle, Pacific Northwest Division, Richland, Washington.

Fiskum SK, MJ Steele, and DL Blanchard, Jr. 2006b. Small Column Ion Exchange Testing of Spherical Resorcinol-Formaldehyde Resin for ^{137}Cs Removal from Pre-Treated Hanford Tank 241-AN-102 Waste (Envelope C). PNWD-3751, Battelle, Pacific Northwest Division, Richland, Washington.

Fiskum SK, IE Burgeson, OT Farmer, III, LR Greenwood, CZ Soderquist, MJ Steele, and MP Thomas. 2006c. *Spherical Resorcinol-Formaldehyde Resin Analysis Following Actual Hanford Tank Waste Processing*. PNWD-3752, Battelle, Pacific Northwest Division, Richland, Washington.

Flach GP and FG Smith III. 2013. *Degradation of Cementitious Materials Associated with Saltstone Disposal Units*. SRNL-STI-2013-00118, Rev. 1, Savannah River National Laboratory, Aiken, South Carolina.

Fox KM, DK Peeler, JM Pareizs, CL Crawford, and TB Edwards. 2014. *Evaluation of Defense Waste Processing Facility (DWPF) Glass Samples After an Extended Melter Outage*. SRNL-STI-2014-00302, Savannah River National Laboratory, Aiken, South Carolina.

Gauglitz PA and G Terrones. 2002. *Estimated Maximum Gas Retention from Uniformly Dispersed Bubbles in K-Basin Sludge Stored in Large-Diameter Containers*. PNNL-13893, Pacific Northwest National Laboratory, Richland, Washington.

Geeting JGH and RT Hallen. 2005. "Filtration, Washing, and Caustic Leaching of Hanford Tank AZ-101 Sludge." *Separation Science and Technology* 40(1-3): 1–15.

Gilmore T, BB Looney, N Cutshall, D Major, T Wiedemeier, FH Chappelle, M Truex, T Early, M Heitkamp, J Waugh, D Peterson, G Wein, C Bagwell, M Ankeny, K Vangelas, KM Adams, and CH Sink. 2006. *Characterization and Monitoring of Natural Attenuation of Chlorinated Solvents in Ground Water:*

A Systems Approach. WSRC-STI-2006-00084, Rev. 1, Washington Savannah River Company, Savannah River Site, Aiken, South Carolina, http://sti.srs.gov/fulltext/WSRC-STI-2006-00084.pdf.

Gin S, A Abdelouas, LJ Criscenti, WL Ebert, K Ferrand, T Geisler, MT Harrison, Y Inagaki, S Mitsui, KT Mueller, JC Marra, CG Pantano, EM Pierce, JV Ryan, JM Schofield, CI Steefel, and JD Vienna. 2013. "An International Initiative on Long Term Behavior of High Level Nuclear Waste Glass." *Materials Today* 16(6): 243–248.

Grambow B. 1985. "A General Rate Equation for Nuclear Waste Glass Corrosion." *MRS Proceedings* 44: 15–27, Scientific Basis for Nuclear Waste Management.

Hallen RT, IE Burgeson, FV Hoopes, and DR Weier. 2002. *Optimization of Sr/TRU Removal Conditions with Samples of AN-102 Tank Waste*. PNWD-3141, Battelle, Pacific Northwest Division, Richland, Washington.

Hazen TC, B Faybishenko, and P Jordan. 2008. *Complexity of Groundwater Contaminants at DOE Sites*. LBNL-4117E, Lawrence Berkley National Laboratory, Berkley, California.

Herman D, M Poirier, M Fowley, M Keefer, T Huff, W Greene, and J Gilmour. 2011. "Testing of the Second Generation SpinTek Rotary Filter." In *WM2011 Conference Proceedings*, March 7–11, 2011, Phoenix, Arizona.

Hobbs DT, MJ Barnes, RL Pulmano, KM Marshall, TB Edwards, MG Bronikowski, and SD Fink. 2005. "Strontium and Actinide Separations from High Level Nuclear Waste Solutions using Monosodium Titanate 1. Simulant Testing." *Separation Science and Technology* 40(15): 3093–3111.

Hobbs DT, RL Messer, JB Lewis, DR Click, PE Lockwood, and JC Wataha. 2006. "Adsorption of Biometals to Monosodium Titanate in Biological Environments." *Journal of Biomedical Materials Research Part B: Applied Biomaterials* 78(2): 296–301.

Hoffman EN, PE Zapp, BJ Wiersma, and TB Edwards. 2010. "Probability-Based Corrosion Control for High Level Waste Tanks." Presented at *CORROSION 2010*, March 14–18, 2010, NACE International, San Antonio, Texas.

Hrma P, J Matyas, and DS Kim. 2003. "Evaluation of Crystallinity Constraint for HLW Glass Processing." *Environmental Issues and Waste Management Technologies in the Ceramic and Nuclear Industries VIII* 143: 133–140.

IAEA – International Atomic Energy Agency. 2012. *Storage of Spent Nuclear Fuel*. IAEA Safety Standards Series, SSG-15, International Atomic Energy Agency, Vienna, Austria.

Izatt RM, JS Bradshaw, and RL Bruening. 1999. "Ion Separation in Membrane and Solid Phase Extraction Systems." In DN Reinhoudt (ed.) *Perspectives in Supramolecular Chemistry: Supramolecular Materials and Technologies*, volume 4, chapter 6, pp. 225, John Wiley & Sons, New York.

Jenkins KD, YN Deng, and SL Orcutt. 2012. *2012 WTP Tank Utilization Assessment*. 24590-WTP-RPT-PE-12-001, Rev. 0, River Protection Project, Hanford Tank Waste Treatment and Immobilization Plant, Richland, Washington.

Johnson ME and TW Crawford. 2000. *River Protection Project Waste Treatment Plant Development Requirements Document*. PL-W375-TE00002, Rev. 1, CH2MHILL Hanford Group, Inc., Richland, Washington.

Kim DS, DK Peeler, and P Hrma. 1995. "Effects of Crystallization on the Chemical Durability of Nuclear Waste Glasses," *Ceramic Transactions Series* 61: 177–185.

Kim D, MJ Schweiger, CP Rodriguez, WC Lepry, JB Lang, JV Crum, JD Vienna, FC Johnson, JC Marra, and DK Peeler. 2011. *Formulation and Characterization of Waste Glasses with Varying Processing Temperature*. PNNL-20774 (EMSP-RPT-009), Pacific Northwest National Laboratory, Richland, Washington.

Kim DS, MJ Schweiger, WC Buchmiller, and J Matyas. 2012. *Laboratory-Scale Melter for Determination of Melting Rate of Waste Glass Feeds*. PNNL-21005, Pacific Northwest National Laboratory, Richland, Washington.

Kim DS and JD Vienna. 2012. *Preliminary ILAW Formulation Algorithm Description*. 24590-LAW-RPT-RT-04-0003, Rev. 1, ORP-56321, River Protection Project, Hanford Tank Waste Treatment and Immobilization Plant, Richland, Washington.

King WD, NM Hassan, DJ McCabe, LL Hamm, and ME Johnson. 2001. *Technetium Removal from Hanford and Savannah River Site Actual Tank Waste Supernates with SuperLig® 639 Resin*. WSRC-MS-2001-007609, Westinghouse Savannah River Company, Aiken, South Carolina.

Kurath DE, DL Blanchard, and JR Bontha. 1999. *Ion Exchange Distribution Coefficients for ^{137}Cs and ^{99}Tc removal from Hanford Tank Supernatants AW-101 (Envelope A) and AN-107 (Envelope C)*. PNWD-2467, Battelle, Pacific Northwest Division, Richland, Washington.

Kurath DE, DL Blanchard, and JR Bontha. 2000. *Small Column Ion Exchange Testing of Superlig® 644 for Removal of ^{137}Cs from Hanford Tank Waste Envelope A (Tank 241-AW-101)*. PNWD-3001, Battelle, Pacific Northwest Division, Richland, Washington.

Langton C and M Dukes. 1984. "Defense Waste Salt Disposal at the Savannah River Plant." In *Waste Management Symposia*, March 11-15, 1984, Phoenix, Arizona.

Li H, JD Vienna, P Hrma, DE Smith, and MJ Schweiger. 1997. "Nepheline Precipitation in High Level Waste Glasses: Compositional Effects and the Impact on the Waste Form Acceptability." *MRS Proceedings* 465: 261–268, Symposium II, Scientific Basis for Nuclear Waste Management XX.

Lynch R, R Dosch, B Kenna, J Johnstone, and E Nowak. 1976. "The Sandia Solidification Process – A Broad Range Aqueous Solidification Method." *IAEA Symposium on the Management of Radioactive Waste*, Vienna, Austria, March 22–26, 1984, pp. 360–372.

Marsh F, ZV Svitra, and SM Brown. 1995. *Effects of Soluble Organic Complexants and Their Degradation Products on the Removal of Selected Radionuclides from High-Level Waste. Part I, LA-12862, Part II, LA-12943, and Part III and Part IV.* LA-13000, Los Alamos National Laboratory, Los Alamos, New Mexico.

McCabe DJ, NM Hassan, WD King, JL Steimke, MA Norato, LL Hamm, and LN Oji. 2000. *Comprehensive Scale Testing of the Ion Exchange Removal of Cesium and Technetium from Hanford Tank Wastes*. WSRC-MS-2000-00499, Westinghouse Savannah River Company, Aiken, South Carolina.

McCloy JS and JD Vienna. 2010. *Glass Composition Constraint Recommendations for Use in Life-Cycle Mission Modeling*. PNNL-19372, Pacific Northwest National Laboratory, Richland, Washington.

Michalske T. 2014, July 15. Presentation on behalf of the National Laboratory Director's Council Task Force to the Secretary of Energy Advisory Board.

Moyer BA, PV Bonnesen, LH Delmau, FV Sloop, Jr., NJ Williams, JF Birdwell, Jr., DL Lee, RA Leonard, SD Fink, TB Peters, and MW Geeting. 2011. "Development of the Next-Generation Solvent Extraction (NG-CSSX) Process for Cesium Removal from High-Level Tank Waste-11346." In *WM2011 Conference Proceedings*, February 27–March 3, 2011, Phoenix, Arizona.

Moyer BA, LH Delmau, NC Duncan, DD Ensor, TG Hill DL Lee, BD Roach, FV Sloop, Jr., and NJ Williams. 2013. *Recommended Guidance Suppressor for the Next-Generation Caustic-Side Solvent Extraction Process.* ORNL/TM-2012/625, Oak Ridge National Laboratory, Oak Ridge, Tennessee.

Nash CA, HH Saito, and WR Wilmarth. 2003. "Strontium and Transuranic Precipitation and Crossflow Filtration of a Large Hanford Tank 241-AN-102 Sample." *Separation Science and Technology* 38(12-13): 3189–3213.

Nash, C. A.; Saito, H. H.; Wilmarth, W. R. "Strontium and transuranic precipitation and crossflow filtration of a large Hanford Tank 241-AN-102 sample," Sep. Sci. Technol. 2003, 38, 3189–3213.

NRC – National Research Council. 1996. Environmental Management Technology-Development Program at the Department of Energy 1995 Review. National Academies Press, Washington, DC.

NRC – National Research Council. 1999. Technologies for Environmental Management: The Department of Energy's Office of Science and Technology. National Academies Press, Washington, DC.

NRC – National Research Council. 2000. Research Needs in Subsurface Science: US Department of Energy's Environmental Management Science Program. National Academies Press, Washington, DC.

NRC – National Research Council. 2001. *Science and Technology for Environmental Cleanup at Hanford*. National Academies Press, Washington, DC.

NRC – National Research Council. 2009. *Advice on the Department of Energy's Cleanup Technology Roadmap: Gaps and Bridges*. National Academies Press, Washington, DC.

Nyman M and DT Hobbs. 2006. "A Family of Peroxo-titanate Materials Tailored for Optimal Strontium and Actinide Sorption." *Chemistry of Materials* 18(26): 6425–6435.

Oji LN, DP Diprete, CJ Coleman, MS Hay, and EP Shine. 2012a. *Analysis of Tank 6F Final Characterization Samples – 2012*. SRNL-STI-2012-00365, Rev. 0, Savannah River National Laboratory, Aiken, South Carolina.

Oji LN, DP Diprete, CJ Coleman, and MS Hay. 2012b. *Analysis of Tank 5F Final Characterization Samples – 2011*. SRNL-STI-2012-00034, Rev. 1, Savannah River National Laboratory, Aiken, South Carolina.

Oji LN, DP Diprete, CJ Coleman, MS Hay, and EP Shine. 2014. *Tank 16H Residual Sample Analysis Report*. SRNL-STI-2014-00321, Rev. 1, Savannah River National Laboratory, Aiken, South Carolina.

Pegg IL. 2015. “Behavior of Technetium in Nuclear Waste Vitrification Processes.” *Journal of Radioanalytical and Nuclear Chemistry* 305(1): 287–292. DOI: 10.1007/s10967-014-3900-9.

Peters TB, MJ Barnes, DT Hobbs, DD Walker, FF Fondeur, MA Norato, and SD Fink. 2006. “Strontium and Actinide Separations from High Level Nuclear Waste Solutions using Monosodium Titanate 2. Actual Waste Testing.” *Separation Science and Technology* 41(11): 2409–2427.

Peters TB, MR Poirier, and SD Fink. 2010. “Processing Macrobatch 2 at the Savannah River Site Integrated Salt Disposition Process.” *Separation Science and Technology* 45: 1801–1806.

Rassat SD, SM Caley, PR Bredt, PA Gauglitz, DE Rinehart, and SV Forbes. 1998. *Mechanisms of Gas Bubble Retention and Release: Experimental Results for Hanford Single Shell Waste Tanks 241-A-101,241-S-106, and 241-U-103*. PNNL-11981, Pacific Northwest National Laboratory, Richland, Washington.

Reed S and J James. 2010. *Environmental Restoration Overview - Mountain Creek Industrial Center*. Naval Facilities Engineering Command Southeast, Jacksonville, Florida.

Riley RG, JM Zachara, and FJ Wobber. 1992. *Chemical Contaminants on DOE Lands and Selection of Contaminant Mixtures for Subsurface Science Research*. DOE/ER-0547T (DE92 014826), US Department of Energy Research, Subsurface Science Program, Washington, DC.

Rimando R. 2015. Personal communication.

Russell RL, JM Billing, HD Smith, and RA Peterson. 2009. “Validation of Ultrafilter Performance Model Based on Systematic Simulant Evaluation.” *Industrial & Engineering Chemistry Research* 48(22): 10077–10086.

Schonewill PP, RC Daniel, RR Russell, RW Shimskey, CA Burns, JM Billing, BM Rapko, and RA Peterson. 2012. “Development of an S-Saltcake Simulant Using Crossflow Filtration as a Validation Technique.” *Separation Science and Technology, Special Issue: Seventeenth Symposium on Separation Science and Technology for Energy Applications* 47(14-15): 2098–2107.

Schulz WW and LA Bray. 1987. “Solvent Extraction Recovery of Byproduct ^{137}Cs and ^{90}Sr from HNO_3 solutions—A Technology Review and Assessment.” *Separation Science and Technology* 22(2-3): 191–214.

SEAB – Secretary of Energy Advisory. 2014. *Report of the Task Force on Technology Development for Environmental Management*. US Department of Energy, Washington, DC.

Serne RJ, BM Rapko, and IL Pegg. 2014. *Technetium Inventory, Distribution, and Speciation in Hanford Tanks*. PNNL-23319, Rev. 1, Pacific Northwest National Laboratory, Richland, Washington.

Spence RD and C Shi. 2005. Stabilization and Solidification of Radioactive and Mixed Waste. CRC Press: Boca Raton, Florida.

SRNL – Savannah River National Laboratory. 2011. *Demonstration of Long-Term Storage Capability for Spent Nuclear Fuel in L Basin*. SRNL-STI-2-11-00190, Savannah River National Laboratory, Aiken, South Carolina.

Subramanian KH, BJ Wiersma, and PE Zapp. 2008. “Current Corrosion Issues in Radioactive High Level Waste Tanks.” Presented at *CORROSION 2008*, March 16–20, 2008, NACE International, New Orleans, Louisiana.

Thomas S and G Dickert. 2013. “Regulatory Framework for Salt Waste Disposal and Tank Closure at the Savannah River Site.” In *WM2013 Conference Proceedings*, February 24–28, 2013, Phoenix, Arizona.

Thorson M. 2008. Basis of Recommendation for Use of Spherical Resorcinol Formaldehyde Resin as the Primary Cesium Ion Exchange Resin in the WTP. 24590-WTP-RPT-RT-07-005, Bechtel Waste Treatment Plant, Richland, Washington.

Van Iseghem P, M Aertsens, K Lemmens, S Gin, D Deneele, B Grambow, P McGrail, D Strachan, and G Wicks. 2007. A Critical Evaluation of the Dissolution Mechanisms of High Kevel Waste Glasses in Conditions of Relevance for Geological Disposal (GLAMOR). EUR 23097, European Atomic Energy Commission, Brussels, Belgium.

Van Iseghem P, M Aertsens, S Gin, D Deneele, B Grambow, D Strachan, P McGrail, and G Wicks. 2009. “GLAMOR – Or How We Achieved a Common Understanding on the Decrease of Glass Dissolution Kinetics.” *Environmental Issues and Waste Management Technologies in the Materials and Nuclear Industries XII*, eds. A Cozzi and T Ohji, John Wiley & Sons, Inc., Hoboken, New Jersey.

Vienna JD, JV Ryan, S Gin, and Y Inagaki. 2013. “Current Understanding and Remaining Challenges in Modeling Long-Term Degradation of Borosilicate Nuclear Waste Glasses.” *International Journal of Applied Glass Science* 4(4): 283–294.

Vienna JD and DS Kim. 2014. *Preliminary IHLW Formulation Algorithm Description*. 24590-HLW-RPT-RT-05-001, Rev. 1, River Protection Project, Hanford Tank Waste Treatment and Immobilization Plant, Richland, Washington.

Walker JF, Jr., PA Taylor, RD Spence, CO Slater, DD Walker, DF Bickford, SY Lee, SE Aleman, and LL Hammet. 2004. *Small Column Ion Exchange Alternative To Remove ^{137}Cs From Low-Curie Salt Waste: Summary of Phase 1*. ORNL/TM-2003/287, Oak Ridge National Laboratory, Oak Ridge, Tennessee.

Weber WJ. 2014. “Radiation and Thermal Ageing of Nuclear Waste Glass.” *Procedia Materials Science* 7: 237–246.

Westbrook ML, RL Sindelar, and DL Fisher. 2015. “Radiolytic Hydrogen Generation from Aluminum Oxyhydroxide.” *Journal of Radioanalytical and Nuclear Chemistry* 303(1): 81–86.

Wester DW, DL Baldwin, P Berry, KJ Carson, BJ Cook, LP Darnell, JR DesChane, TG Levitskaia, BM Rapko, and CZ Soderquist. 2003. *Ion-Exchange Research in Support of Modular Treatment of Savannah River Site Tank Wastes*. PNNL-45344, 091103B, Pacific Northwest National Laboratory, Richland, Washington.

Wilmarth WR, SW Rosencrance, CA Nash, DP DiPrete, and CC DiPrete. 2001. “Transuranium Removal from Hanford High Level Waste Simulants using Sodium Permanganate and Calcium.” *Journal of Radioanalytical Nuclear Chemistry* 247(3): 501–506.

Zachara JM, CC Ainsworth, GE Brown, Jr., JG Catalano, JP McKinley, O Qafoku, SC Smith, JE Szecsody, SJ Traina, and JA Warner. 2004. “Chromium Speciation and Mobility in a High Level Nuclear Waste Vadose Zone Plume.” *Geochimica et Cosmochimica Acta* 68(1): 13–30

APPENDIX B – AGENDA AND PARTICIPANTS

APPENDIX B
AGENDA AND PARTICIPANTS

WORKSHOP AGENDA

BRN-EM Day 1

Wednesday, July 8, 2015

12:00 – 1:30 PM	Registration

Opening Plenary Session (Moderator: Harriet Kung) – Grand Ballroom A/B

1:30 – 1:40 PM	*Welcome and Workshop Charge* Pat Dehmer, Acting Director DOE Office of Science
1:40 – 2:00 PM	*DOE Environmental Management Perspective* Monica Regalbuto, Associate Principal Deputy Assistant Secretary DOE Office of Environmental Management
2:00 – 2:45 PM	*Plenary Address* Richard Meserve, Covington & Burling LLP Chair of the 2014 Secretary of Energy Advisory Board Task Force on Technology Development for Environmental Management
2:45 – 3:15 PM	Break
3:15 – 3:45 PM	*Keynote Address: Waste Stream Characterization, Transformation, and Separations* Andrew Felmy, Pacific Northwest National Lab
3:45 – 4:15 PM	*Keynote Address: Waste Form* Bill Weber, University of Tennessee
4:15 – 4:45 PM	*Keynote Address: Contaminant Fate and Transport in Geological Environments* Carl Steefel, Lawrence Berkeley National Lab
4:45 – 5:15 PM	*Introduction of Workshop Leadership and Workshop Format/Goals* Sue Clark, Workshop Chair, Pacific Northwest National Lab and Washington State Univ.
5:15 – 7:00 PM	Dinner (on your own)
7:00 – 9:30 PM	Parallel Breakout Sessions Initial Presentations/Discussion (see last page of agenda for details) Panel 1, Waste Stream – White Oak A Panel 2, Waste Form – Forest Glen

Panel 3, Contaminant Fate and Transport – White Oak B
Panel 4, Crosscutting Research – Glen Echo

BRN-EM Day 2

Thursday, July 9, 2015

7:30 – 8:30 AM	Continental Breakfast
8:30 – 10:15 AM	Parallel Breakout Sessions
10:15 – 10:30 AM	Break
10:30 – 12:00 PM	Parallel Breakout Sessions
12:00 – 1:00 PM	Working Lunch (meeting chairs, panel chairs check-in)
1:00 – 3:00 PM	Parallel Breakout Sessions
3:00 – 3:30 PM	Break
3:30 – 5:30 PM	**Interim Plenary Session (Moderators: Sue Clark, Michelle Buchanan, Bill Wilmarth)** **Grand Ballroom A/B** Report on draft PRDs from each panel (30 minutes per panel for presentation/discussion)
	Dinner (on your own)
	Continued panel discussions in the evening (at the discretion of panel co-chairs)

BRN-EM Day 3

Friday, July 10, 2015

7:30 – 8:30 AM	Continental Breakfast
8:30 – 10:30 AM	Parallel Breakout Sessions
10:15 – 10:30 AM	Break (Meeting Chairs, Panel Chairs Check-in)
10:30 – 12:00 PM	Parallel Breakout Sessions
12:00 – 1:00 PM	Working Lunch
1:00 – 3:00 PM	**Final Plenary Session (Moderators: Sue Clark, Michelle Buchanan, Bill Wilmarth)** **Grand Ballroom A/B** Report on PRDs from each panel (30 minutes per panel for presentation/discussion)
3:00 – 3:15 PM	Workshop Concluding Remarks Sue Clark, Workshop Chair

BRN-EM Day 3 (continued)

Friday, July 10, 2015

3:15 PM	Adjourn (except for writing teams)
3:30 – 4:00 PM	Discussion of Report Writing – Meeting Chairs, Panel Co-Chairs, and Writing Teams
4:00 – 6:00 PM	Parallel Writing Session – Writing Teams
	Dinner (on your own)

BRN-EM Day 4

Saturday, July 11, 2015

7:30 – 8:30 AM	Continental Breakfast
8:30 – 10:15 AM	Parallel Writing Session – Writing Teams
10:15 – 10:30 AM	Break
10:30 – 12:00 PM	Parallel Writing Session – Writing Teams
12:00 – 12:30 PM	Closeout – Meeting Co-Chairs and All Writing Teams
	Adjourn

Breakout Session Presentations (Wednesday, July 8, 7:00 – 9:30pm)

Panel 1 – Waste Stream Characterization, Transformation, and Separations

1. *Hanford and Savannah River Site Waste Processing - A Summary of Similarities and Differences*
   Reid Peterson, PNNL
2. *EM Separations Challenges and Opportunities*
   Gregg Lumetta, PNNL
3. *Short and Long Term Considerations of Radionuclide Speciation in Waste Streams*
   Brian Powell, Clemson Univ.
4. *Microfluidic Separations for Actinide Processing and Analysis*
   Becky Chamberlin, LANL
5. *Low-Energy Electron Scattering: A Link between Fundamental Science and Radioactive Waste Containment Problems*
   Thom Orlando, Georgia Tech

Panel 2 – Waste Form

1. *Value of Thermochemical Understanding and Modeling of Nuclear Waste Forms*
   Ted Besmann, Univ. of South Carolina
2. *Accelerated Aging and Accelerated Dynamics of Nuclear Waste Form Evolution*
   Blas Uberuaga, LANL
3. *In Situ Characterization of Environmental Degradation of Materials*
   Ian Robertson, Univ. of Wisconsin
4. *Waste Storage System Corrosion Issues*
   Narasi Sridhar, DNV GL

Panel 3 – Contaminant Fate and Transport in Geological Environments

1. *Why Little Matters: Fluid-Mineral Interactions from Mineral and Microbial Surfaces to the Pore Scale*
   John Bargar, SLAC
2. *Contaminants, Compliance, and Caveats: Hydro-Biogeochemistry at the Floodplain Scale*
   Ken Williams, LBNL
3. *Geophysical Characterization and Monitoring of Contaminant Fate and Transport: Opportunities, Challenges and Prior Pitfalls*
   Lee Slater, Rutgers

Panel 4 – Crosscutting Research

1. *Adding Reactivity to Structure*
   Bill Casey, UC Davis
2. *Modeling the Materials-Environment System: Achievements and Challenges*
   Michael Demkowicz, MIT

WORKSHOP PARTICIPANTS

Name	Institution
Workshop Chair	
Sue Clark	Pacific Northwest National Lab and Washington State University
Workshop Co-Chairs	
Michelle Buchanan	Oak Ridge National Lab
Bill Wilmarth	Savannah River National Lab
Plenary Speakers	
Patricia Dehmer	Acting Director, Office of Science
Richard Meserve	Covington & Burling LLP
Monica Regalbuto	Associate Principal Deputy Assistant Secretary, Office of Environmental Management
Andrew Felmy	Pacific Northwest National Lab
Bill Weber	University of Tennessee
Carl Steefel	Lawrence Berkeley National Lab
Panel 1: Waste Stream Characterization, Transformation and Separations	
Jenifer Braley	*Colorado School of Mines – Panel Lead*
Mark Antonio	*Argonne National Lab – Panel Lead*
Sam Bryan	Pacific Northwest National Lab
Rebecca Chamberlain	Los Alamos National Lab
Ken Czerwinski	TerraPower/University of Nevada- Las Vegas
Lætitia Delmau	Oak Ridge National Lab
David Dixon	University of Alabama
Ross Ellis	Argonne National Lab
Andrew Felmy	Pacific Northwest National Lab/Washington State University
Nathaniel Fisch	Princeton Plasma Physics Lab/Princeton University
Amy Hixon	Notre Dame University
Gregg Lumetta	Pacific Northwest National Lab
Luther McDonald	University of Utah
Thom Orlando	Georgia Tech
Alena Paulenova	Oregon State University
Reid Peterson	Pacific Northwest National Lab
Brian Powell	Clemson University
Ralf Sudowe	University of Nevada-Las Vegas
Justin Walensky	University of Missouri

Name	Institution
Panel 2: Waste Form	
Gerald Frankel	*Ohio State University – Panel Lead*
Jim Marra	*Savannah River National Lab – Panel Lead*
Theodore Besmann	University of South Carolina
Brady Hanson	Pacific Northwest National Lab
Carol Jantzen	Savannah River National Lab
Meimei Li	Argonne National Lab
Elizabeth Opila	University of Virginia
Ivar Reimanis	Colorado School of Mines
Ian Robertson	University of Wisconsin
Kurt Sickafus	University of Tennessee
Bob Sindelar	Savannah River National Lab
Narasi Sridhar	DNV GL
Blas Uberuaga	Los Alamos National Lab
John Vienna	Pacific Northwest National Lab
Bill Weber	University of Tennessee/Oak Ridge National Lab
Panel 3: Contaminant Fate and Transport in Geological Environments	
David Cole	*Ohio State University – Panel Lead*
Susan Hubbard	*Lawrence Berkeley National Lab – Panel Lead*
John Bargar	SLAC National Accelerator Lab
Ian Bourg	Princeton University
Miles Denham	Savannah River National Lab
Young-Shin Jun	Washington University - St. Louis
Annie Kersting	Lawrence Livermore National Lab
Kate Maher	Stanford University
David Moulton	Los Alamos National Lab
Fred Phillips	New Mexico Tech
Eric Roden	University of Wisconsin
Kevin Rosso	Pacific Northwest National Lab
Tim Scheibe	Pacific Northwest National Lab
Lee Slater	Rutgers University
Carl Steefel	Lawrence Berkeley National Lab
Dave Wesolowski	Oak Ridge National Lab
Ken Williams	Lawrence Berkeley National Lab
Kelly Wrighton	Ohio State University
John Zachara	Pacific Northwest National Lab

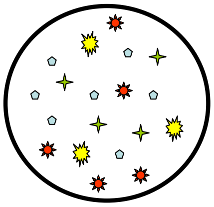
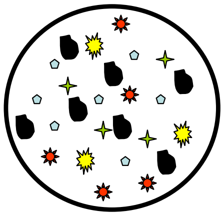
Name	Institution
Panel 4: Crosscutting	
Todd Allen	*Idaho National Lab – Panel Lead*
Aurora Clark	*Washington State University – Panel Lead*
Bill Casey	University of California - Davis
Lynne Ecker	Brookhaven National Lab
Michael Demkowicz	Massachusetts Institute of Technology
Tom Doe	Golder Associates
Maik Lang	University of Tennessee
David Shuh	Lawrence Berkeley National Lab
Department of Energy Participants	
Paul Bayer	Office of Science
Steve Binkley	Office of Science
Pat Dehmer	Office of Science
Gerald Geernaert	Office of Science
Bonnie Gersten	Office of Science
Roland Hirsch	Office of Science
Linda Horton	Office of Science
Harriet Kung	Office of Science
David Lesmes	Office of Science
Natalia Melcer	Office of Science
John Miller	Office of Science
Raul Miranda	Office of Science
Larry Rahn	Office of Science
Andy Schwartz	Office of Science
Michael Sennett	Office of Science
Ceren Suset	Office of Science
John Vetrano	Office of Science
Sharlene Weatherwax	Office of Science
Philip Wilk	Office of Science
Tanja Pietrass	Office of Science
Kurt Gerdes	Office of Environmental Management
Mark Gilbertson	Office of Environmental Management
Dinesh Gupta	Office of Environmental Management
Dennis Koutsandreas	Office of Environmental Management
Nicholas Machara	Office of Environmental Management
Justin Marble	Office of Environmental Management
John Marra	Office of Environmental Management
Monica Regalbuto	Office of Environmental Management
James Shuler	Office of Environmental Management

Name	Institution
Karen Skubal	Office of Environmental Management
Mathew Zenkowich	Office of Environmental Management
Observers	
James Bresee	Office of Nuclear Energy
Phillip Britt	Oak Ridge National Lab
Jalena Dayvault	Office of Legacy Management
Anne Gaffney	Idaho National Lab
Bruce Garrett	Pacific Northwest National Lab
Kimberly Grey	Office of Nuclear Energy
Chris Gunther	National Energy Technology Lab
Naomi Jaschke	Richland Operations Office
Paul Kalb	Brookhaven National Lab
Bob Kephart	Fermi National Accelerator Lab
Billie Mauss	Office of River Protection
Roger Nelson	Waste Isolation Pilot Plant
Patricia Paviet	Office of Nuclear Energy
Elizabeth Phillips	Oak Ridge Office of Environmental Management
Don Reed	Los Alamos National Lab
Natalis Saraeva	Argonne National Lab
Henry Shaw	Lawrence Livermore National Lab

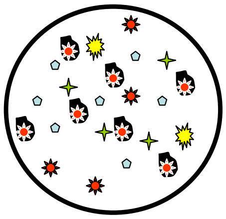
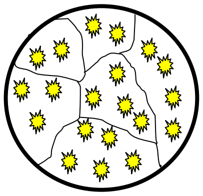
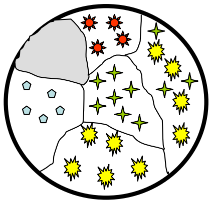
APPENDIX C – SUMMARY OF WASTE FORM MATERIALS

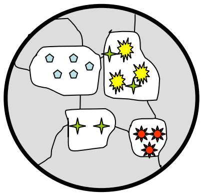
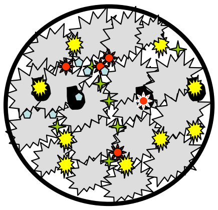
APPENDIX C
SUMMARY OF WASTE FORM MATERIALS

Legacy radioactive wastes must be processed by the US Department of Energy Environmental Management and stabilized into waste forms for disposal. The waste form materials must incorporate and/or encapsulate the processed wastes, ideally retaining the contaminants for millennia. Different types of waste forms offer different retention mechanisms, waste loadings, and durability. Linking waste processing schemes with waste form characteristics is essential for producing effective and resilient waste disposal strategies. The table serves as a primer for considering types of waste forms in the context of waste stream attributes and disposal requirements.

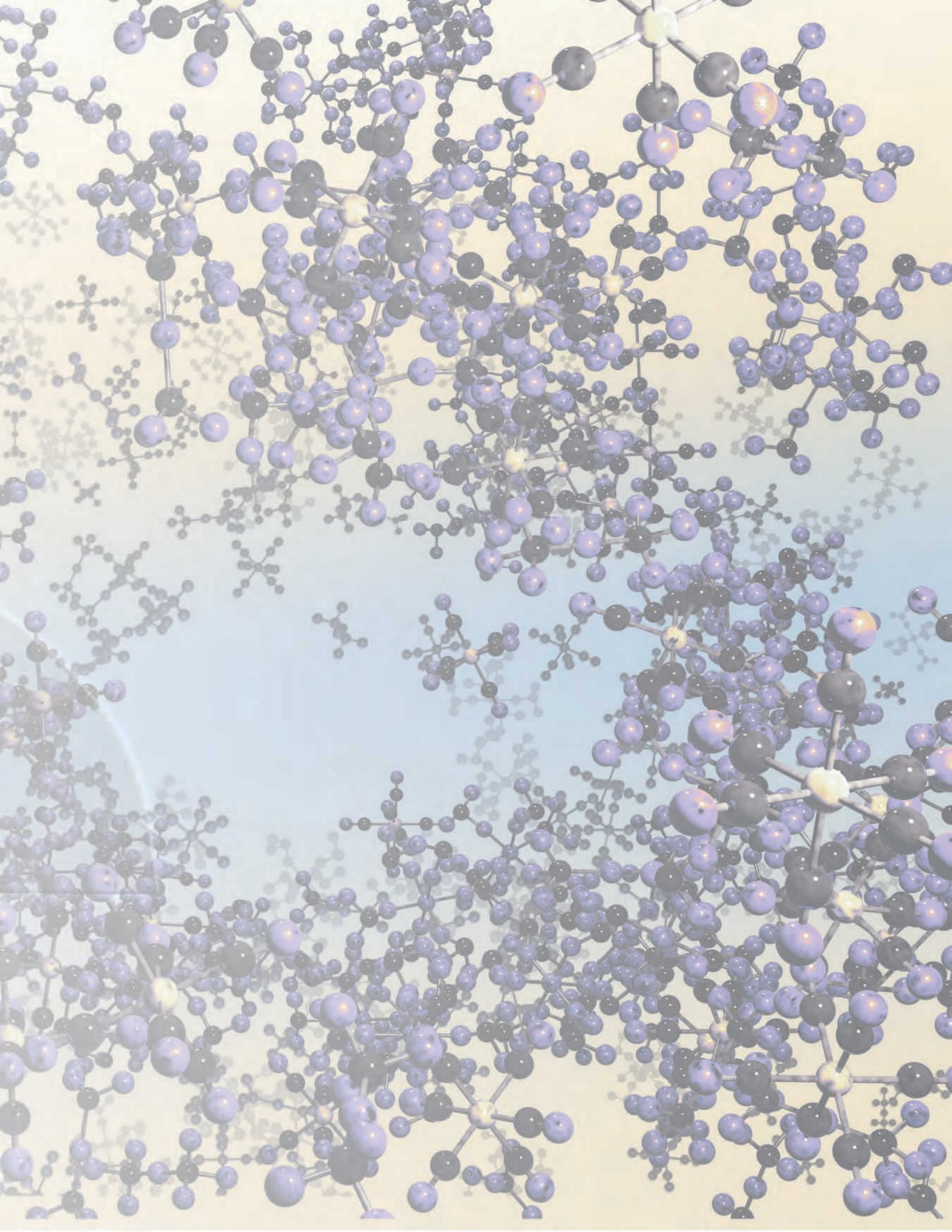
Waste Form	Retention Mechanism	Pictorial of Incorporation Mechanism	Waste Loading/ Overall Durability	Examples
Single Phase Glasses Radioactive and hazardous species are atomically bonded in the glass structure usually to oxygens that are also bonded to the matrix elements, Si, Al, B, P, etc., by short range order and medium range order.	Chemical Incorporation		Loading: Moderate Durability: Good Modeling: Easy to model radionuclide release from a single phase	Borosilicate glasses, aluminosilicate glasses, phosphate glasses
Glass Ceramic Material Radioactive and hazardous species are in the glassy matrix (like single phase glasses). Benign crystals such as spinels (Cr, Ni, Fe species) are allowed to crystallize (●). The spinels do not contain radionuclides but may sequester hazardous species.	Chemical Incorporation		Loading: Higher for high Cr, Ni, Fe wastes Durability: Good Modeling: Easy for radionuclide release from single phase glass as minimal impact from grain boundary dissolution (must be determined by experiment)	Higher waste loaded borosilicate, aluminosilicate, or phosphate glasses

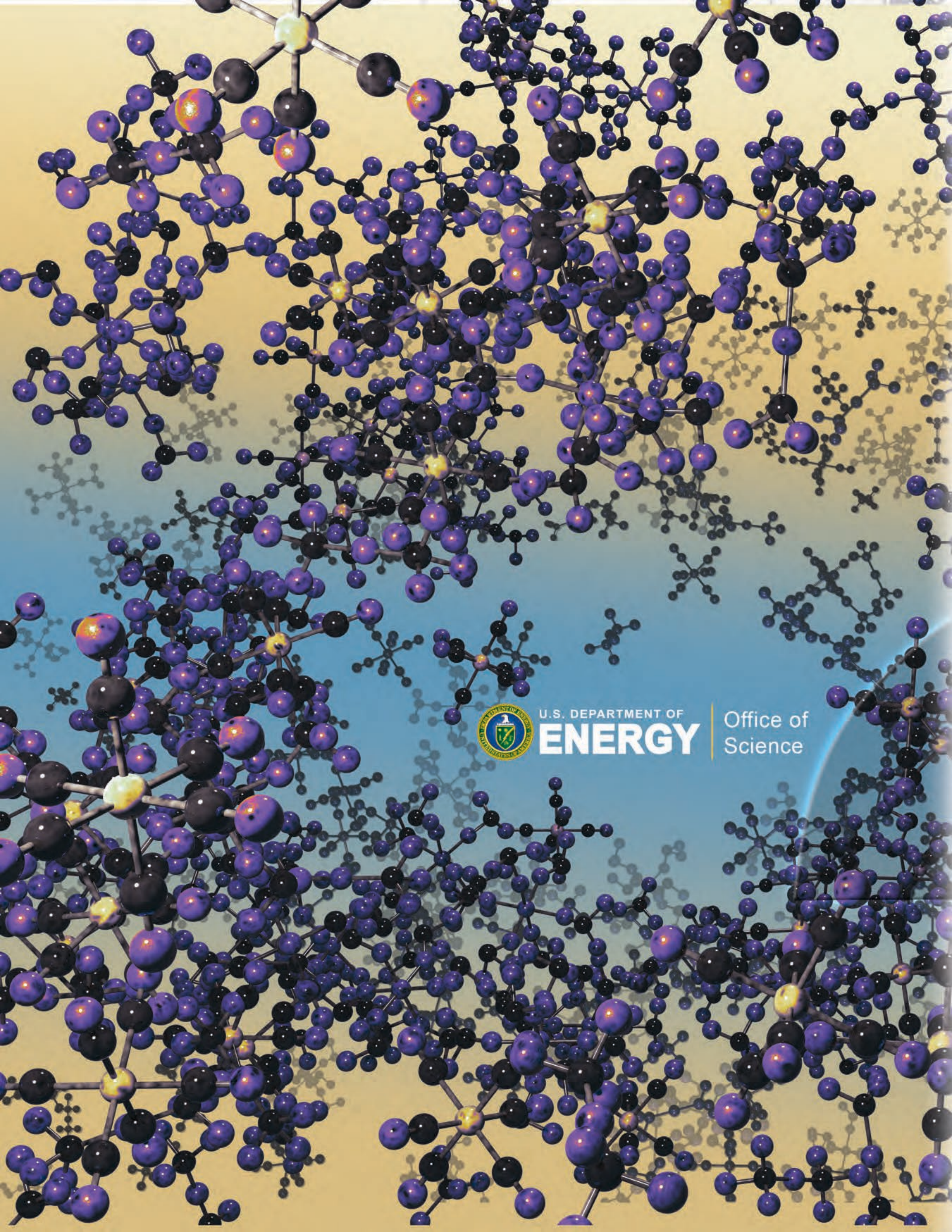
APPENDIX C – SUMMARY OF WASTE FORM MATERIALS

Waste Form	Retention Mechanism	Pictorial of Incorporation Mechanism	Waste Loading/ Overall Durability	Examples
Glass Ceramic Material Radioactive and hazardous species are in the glass matrix and in the crystalline phases. Example shows Cs in the glass and in a secondary phase (●). Secondary phase could be more soluble than the glass, e.g., $(Na,Cs)_2SO_4$, or more durable than the glass, e.g., pollucite $(Cs,Na)_2Al_2Si_4O_{12}$.	Chemical Incorporation and Encapsulation		Loading: Higher if soluble radionuclide phases are not formed Durability: May be greater or poorer than homogeneous glass Modeling: More complex to model radionuclide release from multiple phases (glass and crystal) and grain boundaries (has to be determined by experimentation)	Glass-bonded sodalite
Crystalline Ceramics – Single Phase **Metals – Single Phase** Multi-grained but only one main phase and each grain contains the same radionuclide(s). Granular or monolithic.	Chemical Incorporation		Loading: High for a single radionuclide of concern Durability: Good Modeling: Easy for radionuclide release from a single phase	Pyrochlores for single actinide stabilization, zeolites for single radionuclide stabilization
Crystalline Ceramics – Multi-Phase **Metals – Multi-Phase** Individual phases contain one or more radionuclides (see solid solution indicated between UO_2 and ThO_2 in one phase). Some phases do not incorporate radionuclides at all (gray shade, no symbols). Granular or monolithic.	Chemical Incorporation		Loading: High Durability: Superior Modeling: Difficult for radionuclide release from multiple phases Processing: Need to tailor for and know radionuclide partitioning among phases Pretreatment: May require pre-calcining for certain processes to work efficiently	SYNROC, tailored ceramics, plutonium ceramics, supercalcines, minerals for multiple actinide stabilization

Waste Form	Retention Mechanism	Pictorial of Incorporation Mechanism	Waste Loading/ Overall Durability	Examples
Granular Crystalline Ceramic or Metal Composites Granular waste forms must be monolithed due to disposal requirements if not containerized. The monolithing agent does not incorporate radionuclides at all (gray shade). Known as composite waste forms (monolithing agents can be numerous-Ca-Si or PO_4 based cements, geopolymers, geopolymeric cements, other binders)	Chemical Incorporation and Encapsulation		Loading: High only if binder (monolithing agent) is minimized Durability: Superior - double containment Modeling: Difficult for radionuclide release from multiple phases Processing: Need to tailor for and know radionuclide partitioning among phases Pretreatment: May require pre-calcining for certain processes to work efficiently	Fluidized bed steam reformer granular product for Hanford Site low-activity waste or Waste Treatment and Immobilization Plant waste in geopolymer matrix
Cements, Geo-polymers, Hydroceramics, Ceramicretes Liquid waste is mixed with concrete or other binder – hydrated phases occur that can incorporate the radionuclides weakly or retain them by sorption. Primary encapsulation is by solidification or precipitation of radionuclides on the grain boundaries where the nonradionuclide containing phases hydrate or crystallize. Example shows technetium sequestered by C-S-H (Ca-Si-OH) hydrates and sequestered by secondary fly ash granules.	Encapsulation		Loading: Low Durability: Lower Modeling: Difficult for radionuclide release from multiple phases and hydrated secondary phases Processing: Easy to process – usually mix and cast	Savannah River Site Saltstone

Key: ✸ Cs ✹ U ⬠ Tc ✦ Pu





U.S. DEPARTMENT OF ENERGY

Office of Science