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Introduction

Materials science is a broad, cross-cutting scientific field, encompassing many disciplines, with chemistry at the heart of it. The central theory behind materials science is looking at the microstructure of a material and how it ties to the larger, molecular, physical and chemical aspects of it.

At SRNL, our materials scientists work to understand and alter the microstructure of materials, customizing or even creating new materials with tailored properties for specific uses. Through the application of science, these new materials have broad applications across the Department of Energy (DOE).

Touching all aspects of SRNL’s DOE mission areas, Materials Science and Technology at SRNL is the driving engine for innovation, providing materials technology and systems solutions to support national security, clean energy development, and further protect the environment. Key SRNL Materials Science and Technology capabilities include:

- Advanced materials synthesis, development, testing and qualification
- Environmental effects on materials
- Corrosion science and technology
- Materials reliability
- Nuclear materials storage, surveillance and processing
- Wasteform formulation for sequestering hazardous constituents

This issue of Matter explores just a few of the materials science efforts underway at SRNL as we put science to work in advancing national security, environmental stewardship and energy manufacturing. This edition includes articles about teaming with Clemson University to advance energy storage; materials and structural monitoring of gas transfer systems and reservoirs; examination of innovative, new materials in our nuclear stockpile; collaborating with other national laboratories to advance the use of cementitious materials, and other innovative and collaborative materials science work at SRNL.

I invite you to peruse this issue of Matter as we significantly play an innovative role in advancing DOE’s mission by providing materials technology and systems solutions.

Dr. Vahid Majidi
Director, SRNL
The Savannah River Site (SRS) is a sprawling 198,000-acre facility located on the edge of the Savannah River in South Carolina. Having a deep-rooted history in scientific discovery, SRNL has played a critical role in many of the innovative approaches used today for operations at SRS. While this publication primarily focuses on current programming within the field of materials science, it is important to understand past contributions of SRNL scientists and engineers at SRS. Highlighted are only five of the many contributions SRNL scientists have made in the field of materials science at SRS.

**Reactor Closure**

When the Cold War ended in 1991, the SRS reactors were shut down. In 2009, SRS permanently decommissioned two reactor facilities plus a test reactor using American Resource Recovery Act funds. The SRS reactor closures had to meet technical, economic, social, and environmental challenges for the residual radioactive material to safely remain at SRS. SRNL materials scientists and engineers designed four flowable Portland cement grouts for the reactor buildings and two flowable low-pH grouts for filling the reactor vessels. Each grout formulation had to account for flowability, long-term stability, set time, heat generation and interactions with materials within the structure. SRNL worked closely with Savannah River Nuclear Solutions (SRNS) to successfully implement these new technologies on a massive scale (over 150,000 cubic meters of flowable grout).

**Defense Waste Processing**

The Defense Waste Processing Facility (DWPF) at SRS is the only operating radioactive waste vitrification plant in the nation. This facility converts radioactive liquid waste currently stored at SRS into a solid glass form suitable for long-term storage and disposal. The processing of this waste required extensive materials compatibility testing coupled with innovative equipment design by SRNL materials scientists and engineers. SRNL used materials science expertise to understand and predict the behavior of radionuclides in the glass waste form used at DWPF: borosilicate glass. Borosilicate glass incorporates a wide range of elements and has been demonstrated to have long-term stability. SRNL scientists also developed the product control strategies and testing protocols to ensure the glass waste form could be safely stored for thousands of years.
Saltstone
Disposition of over 100,000 million gallons of salt waste generated from dissolving reactor fuel at SRS is essential to the DOE closure mission. To date, over 17 million gallons have been stabilized and solidified in Saltstone and disposed of at SRS.
SRNL materials scientists and engineers developed this robust, ambient temperature cement waste form and high-volume production process (130 gpm and pumpable up to 500 m) in the 1980s. The primary cementitious reagent in Saltstone is quenched slag, a glassy by-product from iron ore refining. Saltstone was the first radioactive waste form based on ground slag. Recently, employing SRNL technical guidance, the Saltstone formulation was adjusted to support higher volume Saltstone processing thereby enabling acceleration of the SRS tank closure mission.

Tritium Enterprise
The SRS Tritium Facilities, part of the National Nuclear Security Administration's (NNSA) operations, are designed and operated to supply and process tritium, an isotope of hydrogen gas and a crucial component in developing nuclear weapons. SRNL is the only technology provider for the SRS tritium processing and gas transfer system loading and testing; SRNL’s competency is of critical importance to the effectiveness of the U.S. nuclear stockpile.
From its inception, SRNL materials scientists and engineers have supported the facility and continue to do so by developing specialized closure welds used for reservoirs; supporting the interrogation of materials that may fail in service and developing new and improved processes; determining the efforts of hydrogen isotopes on stainless steels and polymers, and; assisting with troubleshooting and process development for new materials and concepts.

Cassini and Other Deep Space Missions
SRS produced Pu-238 for the National Aeronautics and Space Administration (NASA) to power deep space missions. In 1995, SRS completed the campaign to supply Pu-238 pellets to fuel NASA’s Cassini Mission. The unmanned expedition to the planet Saturn was launched in 1997 and arrived at the ringed planet in 2004 after a flawless flight.
SRNL materials scientists developed the specifications and processes for preparing the Pu-238 oxide powder into heat sources used as radioisotopic thermoelectric generators to supply electrical power for the deep space missions. They also developed compatible sealing materials and the welding process for the transportation containers allowing radioactive decay to occur while mitigating the potential for contamination. □
Patrick Ward, principal investigator and primary concept inventor, is exploring the use of photoelectrodes for vanadium redox flow batteries (VRFB).
Renewable energy technology advancements have continued to progress over the years, with aims for a more sustainable environment. One particular LDRD project at SRNL is exploring the depths of energy storage systems.

Primary batteries are intended to be used once and then recycled. Vanadium redox flow batteries (VRFB), a rechargeable flow battery, uses vanadium ions in different oxidation states to store chemical potential energy. These VRFBs are a promising solution for grid energy storage and SRNL is exploring the use of photoelectrodes to combine energy conversion and storage for these batteries.

The LDRD project’s primary objective is to develop multicomponent photoelectrodes that can use various wavelengths of light found in the solar spectrum to directly store electrochemical energy in a VRFB.

Currently, the project is investigating the fundamental electron transfer mechanisms for novel photoelectrode nanocomposites. These new materials have yet to be used as photoelectrodes or as a methodology to directly charge a redox flow battery. Previous methodologies have used semiconductors to charge a redox flow battery, which were limited to the UV portion of the solar spectrum.

To produce and evaluate the photoelectrodes, the project is developing an array of different production methodologies and using simulated sunlight to determine the effectiveness of each technique. SRNL researchers recently demonstrated viability of expanding the solar utilization past the UV into the visible spectrum. As a result, broadband solar absorption to produce usable electrons from various wavelengths is achievable.

Next steps for the project include a fully produced and designed photoelectrochemical cell to be used in VRFB. If successful, the photoelectrochemical cell can provide opportunities for cost reduction and increased renewable energy penetration.

Principal investigator and primary concept inventor Patrick Ward explains the goal in enhancing and developing technology for solar conversion and energy storage.

“This capability is new to SRNL and the photoelectrode design concepts are unlike anything ever attempted before,” said Ward. “The key benefits from this project are a deeper understanding of photo-induced electron transfer processes, and the development of solar battery technology that could reduce the cost of renewable energy conversion and storage from solar resources.”

SRNL’s Laboratory Directed Research and Development (LDRD) is focused on advancing the technical capabilities needed for the future success of DOE.
Dr. Krentz is in the Energy Materials group within SRNL's Environmental, Materials, and Energy Sciences Directorate. He works closely with Dr. Scott West in the National Security Directorate and focuses on material embrittlement in the structural parts and pieces of a gas transfer system (GTS) developed to process tritium for the U.S. nuclear stockpile. While the national lab's Defense Programs Technology group looks at the functionality of weapons, Dr. Krentz examines the materials used in new construction of a GTS.

Since the inception of our nuclear weapons program in the 1950s, looking at how tritium, the central component in effective nuclear weapons, deteriorates the materials where it is stored has been a challenge. As tritium radioactively decays, it deposits helium in the microstructures of the steel and other materials around it, exacerbating hydrogen embrittlement of the material. This data is significant to the health and estimated life of current stockpile components and future agency designs.

Dr. Krentz looks at how new and innovative reservoir and gas transfer systems might perform in the field.

“All hydrogen isotopes embrittle metal alloys. We want to know that the stainless steel bottles we store things in won't break,” said Krentz. “The designers need to have good data to say, not only that our bottle is structurally sound right now but, also, to know when, down the line, someone needs to change this bottle, it is safe, and there is no chance that it will develop a crack.”

SRNL is a leader in this area of science, collaborating across directorates and working closely with Sandia National Laboratories in Livermore to ensure material is structurally safe in new weapon designs.

“We work closely with the Materials Test Facility within SRNL and the broader DOE laboratory complex,” said Dr. Garcia Diaz, manager of the Energy Materials group. “The Materials Test Facility does more of the production-type measurements on the effects of tritium on materials and we perform more of the fundamental materials research. While we are not in the same directorate, these efforts are definitely related, and we collaborate with them and other laboratories to ensure the materials used to construct our weapon systems are effective and safe.”

Ask researcher Tim Krentz what he does at SRNL and he will tell you: “I break things to see how they work.”
Using materials science to ensure the continued safe storage of our nation’s nuclear materials has long been a patriotic mission at SRNL. Through the Plutonium Surveillance Program, SRNL continues to serve as a national leader in securing the safe storage of the DOE’s plutonium-bearing materials.

To understand the goal of the program, it is important to understand the timeline for the storage of these materials at SRS. The last production reactor at SRS was shut down in 1992. Two years later, the DOE issued the 3013 Directive for “Stabilizing, Packaging, and Storage of Plutonium-Bearing Materials.” This directive was written to standardize the stabilization, packaging and storage of metals and oxides for at least 50 years or until final disposition. In 2001, plutonium stabilization and packaging at SRS started and within two years the Surveillance and Monitoring program was launched. After the DOE called for all surplus non-pit plutonium to be consolidated at SRS, the 3013 Destructive Evaluation (DE) program started.

Overseeing the surveillance and DE programs is the Materials Identification Surveillance (MIS) group, which consists of team members from SRNL, Savannah River Nuclear Solutions Engineering, Los Alamos National Laboratory and experts from across the DOE. The job of this team is to verify, through materials science and engineering, that plutonium-bearing materials can be safely stored for at least 50 years. Engineers and scientists at SRNL and the MIS have defined a strategy to evaluate the condition of the 3013 storage containers and 9975 shipping packages by using data collected during field and laboratory surveillance.

Specifically, SRNL’s role in the program is to analyze the condition of the containers and shipping packages to assure the Pu oxide is stored safely. The drums are disassembled and each part carefully evaluated for any signs of degradation that could limit the service lifetime. The stainless-steel containers are destructively evaluated and analyzed using multiple microscopy techniques, leak detection and analytical chemistry to determine if there are any signs of stress corrosion cracking or other corrosion mechanisms that could impact the integrity of the cans. In addition, oxide stored in the cans is evaluated to determine the oxide composition and the presence of off gases that could contribute to corrosion. Data are collected, analyzed and reported back to the storage facility and DOE. When an issue arises or is identified, scientists from SRNL and MIS then work together to address the concern.

In addition to the 3013 DE program, materials scientists continue to study plutonium and the environment it is being stored in. This field surveillance allows scientists to test conditions that contribute to the degradation of the stainless-steel canisters. Through database management, SRNL is documenting the performance of stored containers and able to flag potential problems based on shelf-life and surveillance activities.

Through this robust storage and evaluation program, materials scientists at SRNL are helping to ensure the long-term safe storage of nuclear materials at SRS and a safer tomorrow for our country and the world.
During the 1950s, DuPont constructed what is now known as SRS: five heavy-water reactors and support facilities to produce nuclear materials, such as tritium and plutonium-239. Several SRS facilities are largely based on nitric acid chemistry, an aggressive environment to many materials that can lead to corrosion. During construction and early operation of the site, several plant failures involving corrosion occurred, prompting researchers at DuPont and then Savannah River Laboratory (SRL), the predecessor of SRNL, to develop and implement tests and methods to screen materials for intergranular corrosion susceptibility. The goal was to prevent future failures and improve plant construction schedules.

Corrosion science is a materials science discipline covering the mechanisms and methods of corrosive environments, susceptibility, material degradation and control. Corrosion, a naturally occurring chemical and/or electrochemical process, involves the disintegration or breaking down of metals and other materials when exposed to corrosive environments, which can include natural (air, water) or chemical service. Corrosion takes place in a variety of forms:

- **General:** Occurs uniformly over a large exposed surface
- **Galvanic or Two-metal:** Occurs when two dissimilar metals produce an electron flow causing corrosion-resistant metal to corrode and attack the other
- **Crevice:** Occurs within narrow openings, fissures and other shielded areas when exposed
- **Pitting:** Localized and occurs on materials exposed to aggressive environments
- **Stress Corrosion Cracking (SCC):** Occurs when there is a combined and synergistic interaction between tensile stress and a corrosive environment
- **Intergranular:** An aggressive form of corrosion that can occur in specific alloy/service environment combinations

SRNL’s experts in corrosion science research work across program areas and for specialty projects, ultimately applying scientific knowledge to aid in preserving our nation’s infrastructure and providing for a more sustainable future.

Today, SRNL’s Corrosion Evaluation (CE) Program is key in preventing service failures in critical SRS operating facilities, and reducing the release of hazardous, corrosive and/or radioactive materials to the environment. The program also minimizes production costs, schedule impacts and risks to personnel. SRNL’s work on corrosion science is integral to the current and future safe operation and maintenance of spent nuclear fuel storage containers, high-level waste tanks and concentrated solar power systems.

Combating CORROSION

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SRNL Spent Fuel Rod Work, 1960s

During the 1950s, DuPont constructed what is now known as SRS: five heavy-water reactors and support facilities to produce nuclear materials, such as tritium and plutonium-239. Several SRS facilities are largely based on nitric acid chemistry, an aggressive environment to many materials that can lead to corrosion. During construction and early operation of the site, several plant failures involving corrosion occurred, prompting researchers at DuPont and then Savannah River Laboratory (SRL), the predecessor of SRNL, to develop and implement tests and methods to screen materials for intergranular corrosion susceptibility. The goal was to prevent future failures and improve plant construction schedules.

Several of these test methods later became ASTM International Standards, notably ASTM A262 Practice A, B and C. These test methods have been incorporated into a Corrosion Evaluation (CE) program that has been used for many years by SRNL to screen materials used in certain SRS service environments.

Today, SRNL’s Corrosion Evaluation (CE) Program is key in preventing service failures in critical SRS operating facilities, and reducing the release of hazardous, corrosive and/or radioactive materials to the environment. The program also minimizes production costs, schedule impacts and risks to personnel. SRNL’s work on corrosion science is integral to the current and future safe operation and maintenance of spent nuclear fuel storage containers, high-level waste tanks and concentrated solar power systems.
Legacy Waste – Spent Nuclear Fuel

Spent nuclear fuel (SNF) is nuclear fuel that has been irradiated in a nuclear reactor. Spent nuclear fuel from former reactors at SRS, as well as from foreign and domestic research reactor programs, is currently stored safely in an underwater storage basin facility at SRS.

Corrosion degradation by water challenges aluminum-clad SNF and aluminum storage containers used to store the SNF in the SRS basin.

If corrosion begins, the ability to safely handle and maintain the SNF would decline, increasing the risk of exposure to personnel and the environment.

SRNL conducts evaluations using material surveillances and electrochemical (EC) testing. Through remote visual and ultrasonic examinations of the SNF and its containers, the expert staff can evaluate and manage corrosion attack. SRNL partners with Sandia National Laboratories and Pacific Northwest National Laboratory to evaluate and manage corrosion of commercial SNF canisters used for dry storage.

Legacy Waste – Underground Liquid Waste Tanks

SRS has stored radioactive waste in large, underground, carbon steel tanks in support of national defense and U.S. nuclear nonproliferation efforts. High-level waste (HLW) is stored as liquid–sludge mixtures in carbon steel tanks. General and pitting corrosion, as well as stress corrosion cracking (SCC) occurs in these carbon steel tanks. Since the 1960s, SRNL has aided in enhancements to the materials, fabrication methods, and waste chemistry controls to improve the performance and integrity of the waste tanks and reduce the risk of corrosion failure.

As part of DOE’s waste clean-up program, the waste is retrieved and immobilized, the tank is cleaned, and then grouted for long-term closure. This lengthy process requires extension of the tank life and close monitoring of the waste chemistry for the corrosion control program.

High-level waste tanks have a typical service life of 40-60 years and most of the tanks have been in-service for an average of 50 years. As part of DOE’s legacy waste removal program, waste is being retrieved and the tanks will be grouted and decommissioned, a lengthy process requiring extending the life of HLW tanks. SRNL is responsible for tracking changes or deviations for the corrosion control program. SRNL’s evaluation protects the environment and ensures that closure processes proceed as efficiently and safely as possible.

Energy Security – Solar Power

SRNL is partnering with National Renewable Energy Laboratory, Sandia National Laboratories, Israeli Chemicals (ICL), Haynes International, University of South Carolina and the DOE to research materials that would best suit concentrated solar power (CSP) systems, as part of the Solar Energy Technology Office SunShot program.

SRNL’s project within the SunShot program is designed to demonstrate techniques that control corrosion while having limited impact on system alloy properties. SRNL’s expertise in molten salt electrochemistry, corrosion in molten salt environments, and electrochemical processing of nuclear materials all help in developing solutions for corrosion mitigation that support CSP system integrity and ensure safe operation.

Due to high-temperature environments, ranging from 500 - 800 °C, and direct contact of alloys with molten chloride salts, CSP systems are at high risk of corrosion. Testing for corrosion in the CSP systems while in the field is difficult due to this extreme heat, and also the need to maintain inert conditions, as molten chloride salt can cause much more corrosion in the presence of oxygen. SRNL is conducting research and developing designs that would control corrosion while having limited impact on system materials.

A growing field, solar technologies can generate electricity, address grid integration challenges and lower the overall cost of solar energy. Concentrated solar power systems are designed to have a 30-year lifetime with minimal maintenance. SRNL’s efforts are essential in the long-term operation of CSP systems.

Summary

Corrosion degradation can have a significant and lasting impact to the facilities, storage and overall mission of SRS. However, SRNL’s work to develop, evaluate and explore methods to decrease the risk of corrosion in SRS and other facilities has proven to be effective. SRNL’s technological and chemical solutions have increased the lifespan of critical infrastructure and presented opportunities for a sustainable future.
SRNL is recognized as a worldwide leader in the use of cementitious materials for radioactive and hazardous waste stabilization, nuclear facility and high-level waste tank closures, and environmental restoration. SRNL applies a holistic approach to designing, testing and deploying cementitious materials and technologies to address low-activity waste treatment and contaminated facility remedial at SRS.

For over 30 years, SRNL has been designing low-level cementitious waste forms and waste treatment processes; performing long-term risk analyses; and providing testing and consulting to DOE sites and the Office of Environmental Management. These efforts have resulted in final disposal of numerous waste streams including SRS Saltstone.

In 1997, SRNL designed grouts with unique properties and supported implementation strategies for closing two SRS HLW tank closures, the first to be closed in the DOE complex. Since then, additional tanks with ancillary equipment and cooling coils have been stabilized with grout. SRNL technology has also been applied at the Idaho National Laboratory, and at the Hanford site.

Two SRS isotope production reactors and a test reactor were also decommissioned. The below-grade portions of the buildings were stabilized with unique highly flowable grouts designed to minimize placement time, labor exposure to radiation, and cost. This technology has been applied to closing small underground tanks and pipelines at SRS.

SRNL cementitious technology was extended to several SRS legacy basins contaminated with radionuclides and chemicals. Over the years, SRNL has supported environmental restorations at several DOE sites, including an innovative cementitious remediation of a large waste receipt trench involving cementitious grout and an organic chemical grout injection at the Oak Ridge Reservation, and pond sludge stabilization and disposal at the Weldon Springs Site.

Recently, SRNL leveraged cementitious technology expertise to assist other countries in their stabilization efforts. SRNL hosted a cementitious training event sponsored by the International Atomic Energy Agency (IAEA) for a Brazilian researcher tasked with grouting boreholes for disposal of sealed source; presented several lectures at a 2020 IAEA Virtual Training Course on cementitious material used in radioactive waste conditioning; and participated in a multi-week IAEA waste treatment training course in China.

Currently, SRNL is exploring new technologies, approaches, and material substitution opportunities to support DOE. SRNL is supporting assessments of deteriorated concrete and repair strategies, and is working on improved durability for “green” materials (less embodied energy over their design life). SRNL is working on use of alternative materials in concrete and construction materials and is exploring micro-reinforcement of concrete to achieve higher strengths with less cement and thinner concrete elements.

In late 2019, SRNL hosted a Cementitious Materials Technical Exchange to discuss DOE and industry technologies and needs. As a followup, SRNL has developed and hosted SRNL was tasked to develop and host a Cementitious Materials Community of Practice to promote collaborative efforts related to historical, current and emerging cementitious material needs and opportunities.
Our nuclear weapons provide a deterrent that helps to protect our nation, but how do we know if they work? Materials science testing is a central aspect of ensuring the effective operation of our nuclear weapons with SRNL engineers and scientists examining the tritium reservoir and nuclear gas transfer systems within our weapons.

SRNL Principal Technical Advisor Carol Kestin has worked in SRNL's Materials Test Facility (MTF) for 28 years, one of the key groups that work to ensure the integrity of the GTS. She has examined hundreds of reservoirs and GTS components and has developed most of the post-function test evaluation methods and protocols currently in use for GTS.

"We look at welds, heat affected zones, valves and other components, not just for tritium degradation, but looking also for manufacturing defects or anything unusual in the reservoir," said Kestin.

Kestin and the MTF team, a group within SRNL's Defense Programs Technology (DPT), is located inside the Tritium Facility and supports GTS surveillance, a program that helps to verify the performance of weapon components and provides data to the Design Laboratories for use in its annual certification of the systems.

Aging studies on reservoir structural materials is fundamental materials science at work, looking at the combined effects of hydrogen and helium embrittlement and any other flaws in the materials used in the more than 14,000 nuclear weapons stockpile, ensuring they are, and will remain, effective.

The surveillance of weapon components through a series of different tests, both destructive and non-destructive, is essential to ensure the reliability of the overall stockpile. This testing helps to ensure the integrity of the stockpile, allowing the United States to avoid underground testing. The MTF is responsible for the GTS post-function testing portion of this much larger nuclear weapon surveillance mission. The GTS testing within the MTF laboratories includes components randomly selected from the stockpile as well as from the inventory of Life Storage Program assets maintained in the Tritium Facility.

Kestin and her team have been performing materials science testing for decades and, in so doing, have pioneered new materials science technology, expediting the tests and ensuring accuracy.

"Autoradiography is a technique used to image the tritium diffused into stainless steel down to the 1 appm (atomic parts per million) level and measure the depth of tritium penetration," Kestin said. "Kenneth Gibbs from R&D Engineering developed a digital autoradiography system for the MTF that has shortened the time of this test from 24 hours to 10 minutes."

As the nation’s tritium laboratory, SRNL applies materials science to examine the health of the nuclear stockpile as one of its central missions. The data obtained by SRNL in concert with other national laboratories and the DOE contributes to the annual certification of the stockpile, helping to ensure our nation’s safety.
ENERGY STORAGE
Through Materials Science

Energy storage has grown to unprecedented levels of importance as the demand for more technologically advanced, longer lasting, smaller and more portable electronic devices increases.

Dominating the market in energizing these devices is the rechargeable lithium ion battery (LIB). However, an inherent safety risk exists in commercially available LIBs due to their use of liquid electrolytes and separator components. If a solid counterpart can replace the liquid electrolytes, these all-solid-state ionic devices would be safer, more reliable, and become a high-energy alternative, serving as a gateway into thin-film batteries powering ionic devices, like large-scaled batteries for vehicles.

The Science-based Approach


Multiscale Modeling

Model systems for development focus on garnet-like structures because their structure can be influenced using dopants that lead to appreciable bulk lithium-ion conductivity at room temperature. However, details into why the structural transitions occur for the specific dopant used and their optimized concentration are not completely understood. This is when theoretical modeling is used to understand the energetics of incorporation and the thermodynamic stability of the structure versus dopant concentration.

With funding through the LDRD program, SRNL is teaming with Clemson University to address issues that currently limit the understanding and implementation of solid-state ionic materials and devices in energy storage applications. The team is using advanced manufacturing techniques with theoretical modeling to implement a science-based approach in the deposition of thin film ion conductors with controlled microstructures and interfaces. The team is developing a method to understand and tailor polycrystalline materials, which are likely to dominate low-cost and scalable energy storage devices, to accelerate the materials value chain from discovery to deployment. This effort complements SRNL activities in current ionic battery work and current national initiatives on advancing manufacturing.

“...the current academic partnership between SRNL and Clemson University aimed at engineering new solid-state ionic materials and applications guided by data driven modeling and simulation.”

Kyle Brinkman
Professor and Department Chair,
Department of Materials Science,
Clemson University
Materials Synthesis and Characterization

The materials are then synthesized using solution combustion synthesis, which allows for rapid and efficient production of high-phase purity materials, and then characterized using advanced high-temperature oxide melt solution calorimetry at Clemson University.

The electrical properties of the ionic conducting materials are evaluated by electrochemical impedance spectroscopy (EIS) as a function of time, temperature and gas phase environment. This information is essential for the rational design of materials and prediction of their long-term performance and stability.

Advanced Manufacturing

Once optimization of the dopants is complete, the team can fabricate the doped thin films with controlled microstructures using 3D printing, followed by rapid laser sintering. Control of the manufacturing of thin film thickness, as well as the grain size, the orientation of the crystals, and the density is through optimization of the laser sintering process and paste compositions. Thin films prepared by the combined 3D printing and laser sintering are then characterized by Scanning Electron Microscopy (SEM), Transmission Electron Microscopy (TEM) and ionic conductivity by EIS. Experimental data are then correlated to the computational results to optimize materials chemistry and microstructure.

The research by SRNL and Clemson University further advances not only the fundamental understanding of garnet-like materials as potential all solid-state ionic devices, but, also, insight into subsequent materials development opportunities and optimization strategies. The developed advanced manufacturing technique for the fabrication of LLZO (lithium lanthanum zirconium oxide) thin films with high-ionic conductivities will allow SRNL to fabricate electrochemical devices, such as solid-state batteries, micro solid oxide fuel cells, and micro electrochemical sensors.

SRNL Principal Investigator Lindsey Roy shared, “having experiment and theory working in concert to design scalable processing of solid-state ionic materials strengthens the ties among SRNL and Clemson University materials researchers and utilizes the LDRD program to solidify research programs of interest to DOE-SC Basic Energy Sciences and DOE-EERE Vehicle Technologies.”

Kyle Brinkman, professor and department chair, Department of Materials Science, Clemson University, added: “The LDRD program was essential to facilitate the current academic partnership between SRNL and Clemson University aimed at engineering new solid-state ionic materials and applications guided by data driven modeling and simulation.” He added, “This work integrating science, modeling and manufacturing strengthens ongoing joint research programs and is expected to result in new research directions of interest to DOE-SC Basic Energy Sciences, DOE-EERE Vehicle Technologies and the Advanced Research Projects Agency-Energy ARPA-E.”
Glass science and engineering at SRNL is central to the DOE’s management and stewardship of the nation’s nuclear defense and energy programs. SRNL has been pivotal in the design basis, qualification and vitrification of the nation’s legacy waste for more than 30 years. The scale of these nuclear programs has and will continue to result in a significant quantity of radioactive waste. The waste must be processed and treated so radioactive and hazardous constituents become permanently stabilized and safely sequestered from the environment for thousands of years. The material of choice for long-term disposition of highly radioactive waste is glass.

Why Glass?

Glass is the global standard for immobilizing radioactive waste due to its chemical and physical properties. Glass is produced through a vitrification process where waste materials are combined with glass, forming additives at a temperature above melting (~1200°C for alumina borosilicate waste glass) and then cast into containers or canisters. Glass can be engineered to be inert in the most extreme environments; is a rigid solid in its final form; can be processed at moderate temperatures (lower than alternative materials); is compositionally flexible, and; incorporates radionuclide elements into the atomic structure, ensuring greater safety. Together, these attributes make glass the primary waste form material for its overall performance, property and processing characteristics.

Performance Modeling

Fundamental to the principle and acceptance of waste form is an ability to confidently predict the material’s performance well into the future. Also necessary is the ability to process the waste form with a high level of reliability, especially when considering different types of waste, accounting for product and system mismatch, and given the limitations to reprocessing glass. Success in real systems, therefore, requires robust modeling and validation. Historically, SRNL glass scientists and engineers have developed models and carried out the necessary research and development needed to support this vital mission.

Today, the Defense Waste Processing Facility (DWPF) at Savannah River Site is the only large-scale operating facility in the United States processing high-level radioactive waste into glass. During processing, models that help scientists predict liquidus temperatures, viscosity and chemical oxidation potential are essential to the continued operation of the DWPF, while models that can predict elemental release are critical to waste acceptance standards and the ultimate performance of the glass waste form. The DWPF has produced more than 4,000 canisters (about 35 million gallons) of waste glass since 1996 with the help of SRNL glass scientists and their understanding of glass behavior.
Continuing Excellence

The glass science and engineering principles central to continuing the mission of the DWPF have practical applications elsewhere in the DOE. In conjunction with other laboratories, vitrification has been demonstrated as an effective approach to dispose of a wide variety of wastes at SRS and other sites, including Oak Ridge Reservation, Los Alamos National Laboratory, Rocky Flats, Fernald Environmental Management Project, and Hanford. Furthermore, vitrification of non-radioactive wastes identified as hazardous by the U.S. Environmental Protection Agency has successfully been demonstrated. Vitrification of these hazardous wastes renders them non-hazardous, allowing them conceptually to be recycled in commercial applications.

Recently, a new approach was developed by SRNL to predict chemical durability of glass. Historically, durability has been determined to be linked to the presence or accumulation of specific phases (e.g., nepheline) in the glass. This new SRNL model proposes that the residual glass composition, after crystallization, is the critical factor, which can be used to determine glass durability. The Structural Integrity of Residual (SIR) model uses empirically derived relationships determined from calculated non-bridging oxygen content to predict glass durability. The SIR model has been used to successfully identify glass with 20-35 wt % Al2O3, concentrations that would significantly increase the projected waste loading in glass planned for processing at Hanford.

Complementary efforts are accelerating the pace of research on glass corrosion using big data techniques made available through the Accelerated Leaching and Testing of GLASS (ALTGLASS) database. ALTGLASS, which is developed, maintained and distributed by SRNL, provides researchers access to chemical durability data for hundreds of glass compositions. This collection of data enables scientists to use informatics to analyze experimental results to better understand glass corrosion science for improved glass composition design.

Foundations for the Future

The scientific and technical competency underpinning the development of glass at SRNL is driving innovation, collaboration and scientific discovery for the DOE. For example, SRNL recently combined the attributes of glass vitrification technology with the properties of crystalline materials to realize the first scale-demonstration of pouring a ceramic waste form. SRNL glass scientists are also pioneering research in the area of engineered cellular magmatics to develop useful materials from post-consumer waste (e.g., recycled glass in landfills). These novel materials are used in applications ranging from geotechnical fill to advanced filtration media and were recently highlighted in a Fortune magazine article about reverse engineering ancient Roman concrete.

SRNL researchers also remain on the vanguard of waste form development through their leadership role in the Center for Hierarchical Waste Form Materials (CHWM). In collaboration with academia, SRNL applies its unique radiological expertise and creativity to synthesize novel actinide compounds and measure damage in materials resulting from radioactive decay. This information provides a scientific basis to engineer materials with new functions.

These examples are just a few demonstrating the value and relevance of SRNL’s glass research and accumulated experience over decades.
Recognizing the commitment and hard work of our people at SRNL is important to our operation in all fields, including materials science. SRNL salutes our Laboratory Fellows as they share their views on the importance of materials science. Each have been given the distinction of Laboratory Fellow for their outstanding scientific achievements in their field, recognition by their peers, and exceptional accomplishments for SRNL.

“We are excited to recognize these six distinguished individuals for their professional achievement and contributions to SRNL and the nation. This is the highest recognition SRNL gives to its top researchers and engineers.”

Dr. Paul Cloessner
Dr. Cloessner is currently the manager of product engineering. He has more than 30 years of experience in nuclear materials applications supporting nuclear stockpile stewardship, nonproliferation, intelligence and waste processing. He is nationally recognized for his strategic leadership in tritium and gas transfer systems for the nuclear stockpile.

“Over the course of my career in nuclear technology, I have been involved in everything from nuclear fuel manufacturing and nuclear waste forms and production, to testing of nuclear stockpile components. These activities require materials to perform reliably in very demanding applications. I am fortunate to have available the expertise of materials scientists to support my work.”

Mr. Joe Cordaro
Mr. Joe Cordaro began his career at SRNL in 1989 and is recognized across the Department of Energy and internationally as an expert in the areas of nuclear instrumentation, electronics, process control and high-speed data acquisition systems.

“Materials science has been integral to the development of next generation miniature radiation detection devices. SRNL has shown that Carbon Nano Tubes can be used to detect radiation, opening the door for miniaturized radiation sensors.”

Dr. David Diprete
Dr. David Diprete has extensive experience in nuclear chemistry, radiobioassay and radiochemistry, which led to the development and implementation of nuclear measurement projects to support DOE and NNSA.

“Using its collection of exotic radionuclides, the SRNL radiochemistry laboratory collaborates with various universities to synthesize novel radiological materials. The goal of this research is to develop these new families of materials capable of retaining radionuclides in persistent structures.”

Dr. Natraj Iyer
With 40 years of experience in materials science research, and nuclear materials and fuel-cycle management, Dr. Iyer is a recognized expert in fuel-cycle technologies, including spent fuel and plutonium management. He has served in senior technical and management positions in industry and government and has extensive experience working with international partners and regulators in nuclear materials management and in nuclear non-proliferation.

“Materials science provides one the opportunity to work in areas from basic science to application and deployment. As a materials scientist at SRNL, I have had the opportunity to work in diverse areas of applications without having to change a career or employer – everything from materials for hydrogen energy storage; processing of printed circuit boards; stainless steel recycling; corrosion science as it applies to spent fuel, plutonium and waste tanks, and; developing science and technology supporting nuclear non-proliferation and packaging systems for threat reduction.”
Dr. Ralph James

Dr. Ralph James is a renowned leader in the development of semiconductor radiation detectors and instruments, as well as their application to nuclear nonproliferation, environmental monitoring, astrophysics, medical imaging, safeguarding of nuclear materials, oil exploration, remote sensing, dosimetry, and homeland security challenge areas.

“Materials science has played a key role in my research to develop a new class of X- and gamma-ray radiation detectors. Our understanding of the correlations between crystal-growth parameters, optoelectronic properties of as-grown materials, surface processing steps involved in detector fabrication, and device performance paved the way to the emergence of novel sensor technologies exhibiting extraordinary spectroscopic and imaging attributes.”

Dr. Robert “Bob” Sindelar

Dr. Robert “Bob” Sindelar is a leading international expert in nuclear materials science and technology in the broad fields of aging effects and aging management of structures, as well as the application of various materials in nuclear systems.

“A practical challenge to material systems is service-induced degradation, ultimately causing failure. Testing to evaluate materials’ performance, even at severe exposure conditions, and application of aging management tools, serve to keep it going.”
FRONT AND BACK COVERS: Researchers Patrick Ward (back cover) and Lauren Hanna (front cover) conduct spectroscopic measurements of materials under various wavelength illumination.