2010 – Vol. 3

SAVANNAH RIVER NATIONAL LABORATORY

SCIENCE AT WORK

Treatment for Savannah River High Level Waste Salt Solutions

Also in this issue:

Advances in Mass Spectrometry Prepare NNSA for the Future

Modeling Our Energy Future

THE NEXT GENERATION: SRNL Interns

Savannah River National Laboratory welcomes new director, Dr. Terry Michalske

As this issue of Science at Work goes to press, SRNL is awaiting the arrival of our new laboratory director, Terry A. Michalske, Ph.D.

Dr. Michalske, who earned his Ph.D. from Alfred University in Ceramic Science, has more than 30 years of experience in the fields of energy science, solar energy, nanotechnology and biomolecular analysis, principally for Sandia National Laboratories. Most recently at Sandia, he was the Director of Energy and Security Systems, focusing on energy science and technology, systems modeling and optimization, and vulnerability and consequence management for major Department of Energy, Department of Homeland Security and Department of Defense programs.

He was chairman of the 2009 "Formulation of a Bipartisan Energy and Climate Policy: Toward an Open and Transparent Process" workshop at the Woodrow Wilson International Center for Scholars in 2009, as well as editor of the workshop report. He is also the principal author of the "National Nanotechnology Initiative: Research Directions II" workshop report in 2007, and of "Nanoscience Research for Energy Needs" report from the National Nanotechnology Initiative Grand Challenge Workshop.

Dr. Michalske's research awards include the Orton Lecture Award; an R&D 100 award (Interfacial Force Microscope); the Woldemar A. Weyl International Glass Science Award from the International Congress on Glass; and the Ross Coffin Purdy Award from the American Ceramic Society. He was a two-time winner of the DOE/Basic Energy Science Materials Science Award for Outstanding Technological Accomplishment.

SAVANNAH RIVER NATIONAL LABORATORY

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U.S. DEPARTMENT OF ENERGY
Office of Environmental Management

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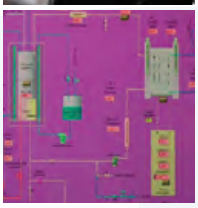

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Treatment for Savannah River High Level Waste Salt Solutions

***The successful startup of the Department of Energy's two newest high-level radioactive** waste treatment processes reflects a 10-year research and technology deployment path, from inception of the basic science to actual radioactive operation. The Actinide Removal Process and the Modular Caustic Side Solvent Extraction Unit will operate over the next several years, reducing the amount of stored waste in the Savannah River Site's tanks and dramatically decreasing the volume of waste that will require expensive high-level waste disposal. More importantly, these modest facilities provide a proving ground for finalizing the design of the Salt Waste Processing Facility. SRNL played the central role in coordinating efforts from across the National Laboratories, universities and industry, leading to implementation of the successful design by the Savannah River Site's liquid waste contractor, Savannah River Remediation.*

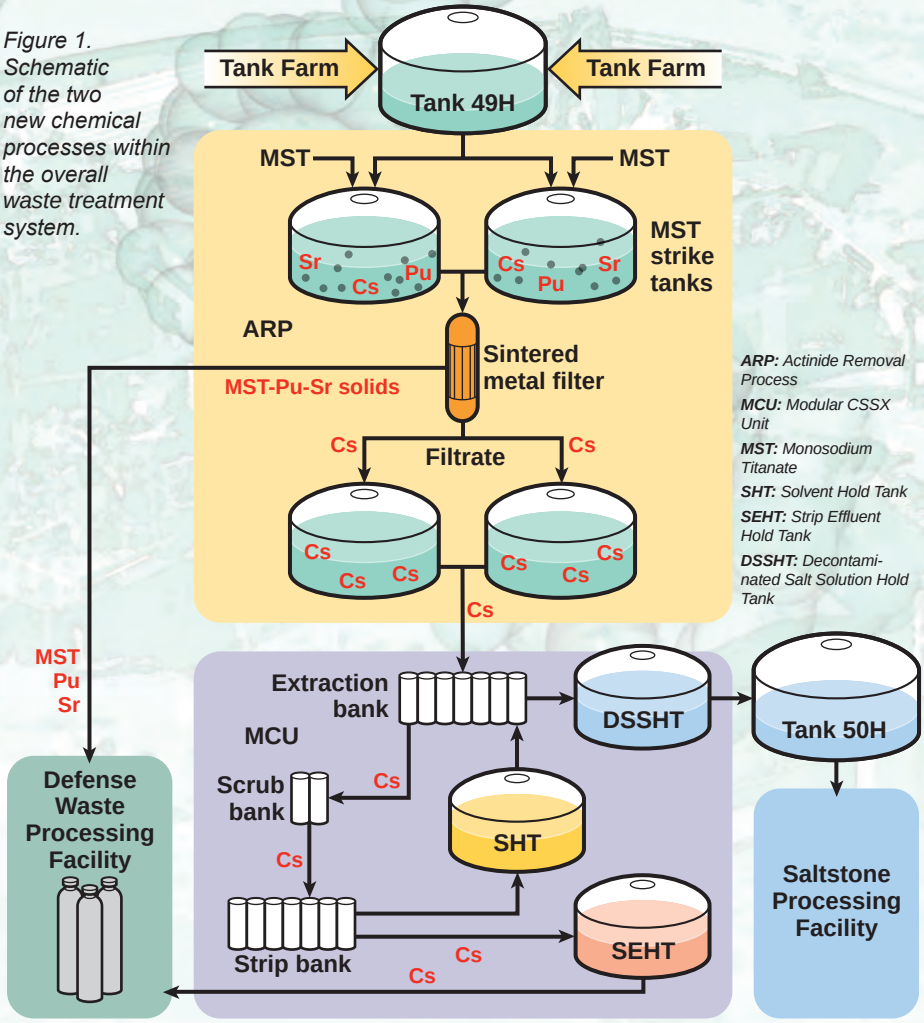


Figure 1. Schematic of the two new chemical processes within the overall waste treatment system.

It's a basic principle of waste management. Two main ways to reduce the time and costs for waste treatment are: make the process more efficient, and reduce the amount of waste to be treated.

At the Savannah River Site (SRS), decades of nuclear material production for the nation's defense resulted in generation of millions of gallons of high-level radioactive liquid waste, now temporarily stored in large underground steel tanks. Since 1996, the site has been converting much of that inventory of waste to a stable glass form, suitable for long-term storage and permanent disposal. Site personnel have worked diligently with Savannah River National Laboratory (SRNL) assistance to make the process highly effective, working toward the optimum balance between speed of processing and quantity of waste per processed canister, while always maintaining the highest levels of safety.

However, existing facilities were unable to process one major type of waste due to the large volumes involved. The answer was to pursue the other line of attack: reduce the amount of waste to be treated by a new process.

Starting in 1998, SRNL, in partnership with other National Laboratories, developed and enhanced a chemical process to treat the SRS High Level Waste (HLW) salt solutions, providing the means to significantly reduce the volume of waste that requires high-level radioactive waste disposal. In April 2008, this technology development and deployment program reached fruition with the initial processing of stored SRS waste through the newest SRS operating facility. The work received funding from the U.S. Department of Energy Office of Basic Energy Sciences, followed by applied research sponsored by the DOE Office of Environmental Management.

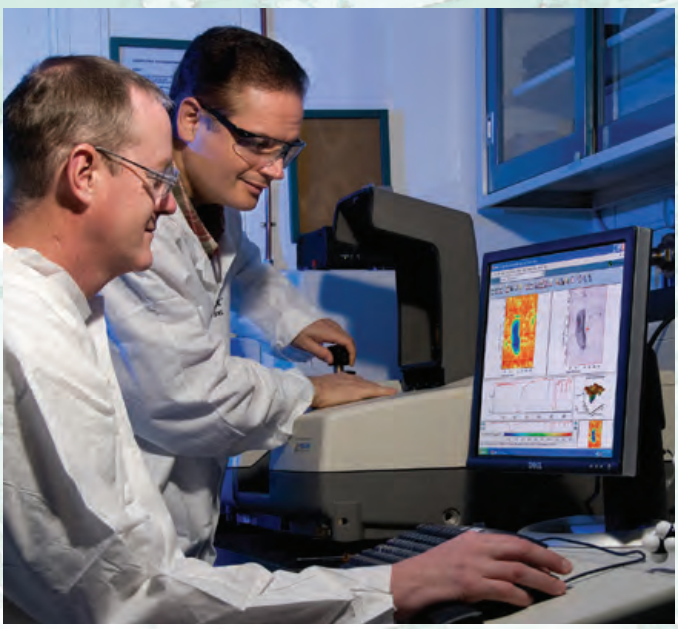
Before being converted to glass, the stored waste is treated to separate the highly radioactive sludge, which makes up about 7 percent of the total volume, from the soluble salts that make up the other 93 percent. This pretreatment produces a large quantity of salt solution containing small amounts of radionuclides - primarily cesium, strontium, and plutonium.

With a process for decontaminating these salt solutions, the radionuclides can be removed and processed with the highly radioactive sludge, leaving the vast majority of the solution clean enough to be handled using much less expensive low-level waste disposal methods.

The SRNL flowsheet combines two processes – the Actinide Removal Process (ARP) and Caustic Side Solvent Extraction (CSSX) - to decontaminate these solutions. As a result, the key radioactive elements are contained in a stream about 1/15th the original volume. The decontaminated waste solution transfers to the Saltstone Production Facility where it is bound in a specialized concrete mixture for disposal. The concentrated radionuclides transfer to the Defense Waste Processing Facility (DWPF) for encapsulation in glass for ultimate disposal (See Figure 1.)

This research program provided essential data for the design and construction of the Salt Waste Processing Facility (SWPF), which will provide a long-term process for treating SRS HLW salt solutions. The program culminated in equipment selection, facility design and construction of both the ARP and the Modular CSSX Unit (MCU), which serve as interim processes for the treatment of SRS salt solutions until completion of the larger scale SWPF. The processes allow DOE to investigate the process chemistry with actual wastes before committing the entire investment for the larger facility.

SRNL's contributions were key to the successful startup of the MCU process. "This has truly been a decade of excellence in research partnering for SRNL. From the inception of the solvent extraction chemistry at Oak Ridge National Laboratory (ORNL) in the late 1990s, SRNL worked steadily at finding the limitations of the solvent chemistry, linking it with the Actinide Removal Process developed locally, and refining the



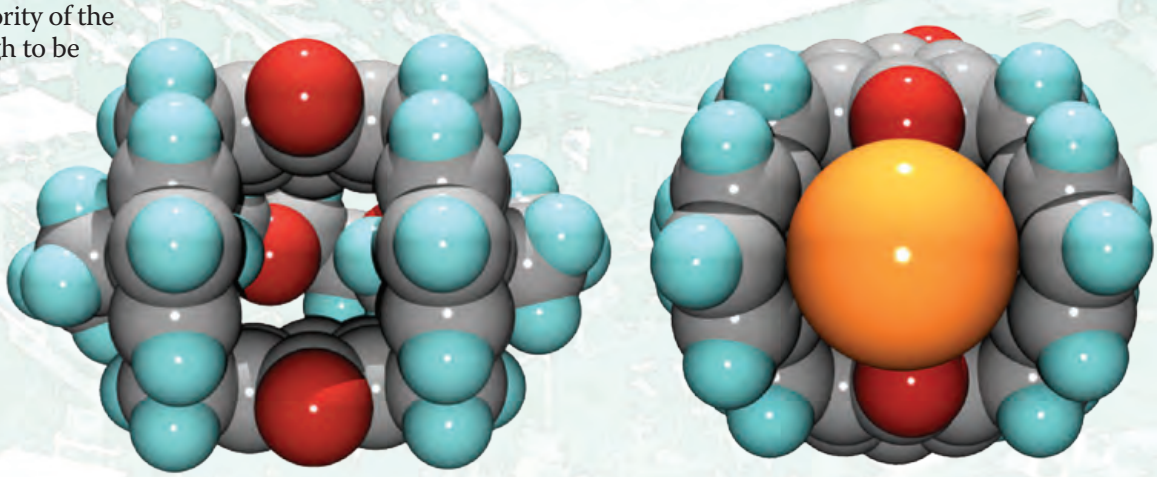


Photo (top): Dr. Fernando Fondeur (right) and Dr. Tom White (left) examine solvent and coalescer media from MCU.

Figure 2. Molecular model of extractant molecule showing captured cesium. Empty cavity (left), and cavity containing cesium ion (right - atoms blocking view of cavity have been removed). Structures courtesy of Oak Ridge National Laboratory.

complete treatment process to match the demands of SRS waste chemistry and facilities," says Dr. Sam Fink, SRNL Separations Science Programs manager who is leading this effort. "SRNL's successful efforts during final deployment built upon the teaming efforts with scientists from ORNL, Argonne National Laboratory (ANL), Pacific Northwest National Laboratory (PNNL) and Idaho National Laboratory, who worked alongside SRNL scientists to develop and enhance the CSSX flowsheet." He adds, "A large number of SRNL personnel supported this important effort over the decade, with leading roles for technical interfaces by: Drs. David Hobbs, Reid Peterson (now with PNNL), Major Thompson, Douglas Walker, Mike Norato (now with the Nuclear Regulatory Commission), Michael Poirier, Tom Peters, and Kofi Adu-Wusu."

The Chemical Process

The ARP, which treats the liquid before it reaches the MCU, removes most (>90%) of the strontium and plutonium from the solution, while also removing some uranium, americium and neptunium. The ARP uses monosodium titanate (MST) particles added to the solution, which sorb the actinides. The solids are then removed by a cross-flow filter designed to remove ~99% of all particles larger than 0.1 micron in effective diameter. These solids, after washing to remove interstitial radioactive solution, transfer to DWPF to be vitrified with the radioactive sludge from the waste tanks. SRNL invested more than two decades in defining the MST and filtration technologies and verifying performance with a wide selection of waste samples.

A second process is needed to remove the radioactive cesium (Cs-137), which gives the salt solutions most of their radioactivity content, to allow processing the solutions as low-level waste using the SRS Saltstone Production Facility. In 2001, the Department of Energy (DOE) and their Technical Advisory Group selected the CSSX process as the preferred method for the separation of Cs-137 from SRS salt solutions.

The CSSX solvent contains a crown ether extractant called Calix[4]arene-bis(tert-octylbenzo-crown-6), also called BOBCalixC6 (Figure 2), which has a high affinity for cesium ions even in the challenging compositions of the SRS waste solutions. After extraction into the solvent phase, cesium can be easily stripped into dilute nitric acid. Another benefit of the

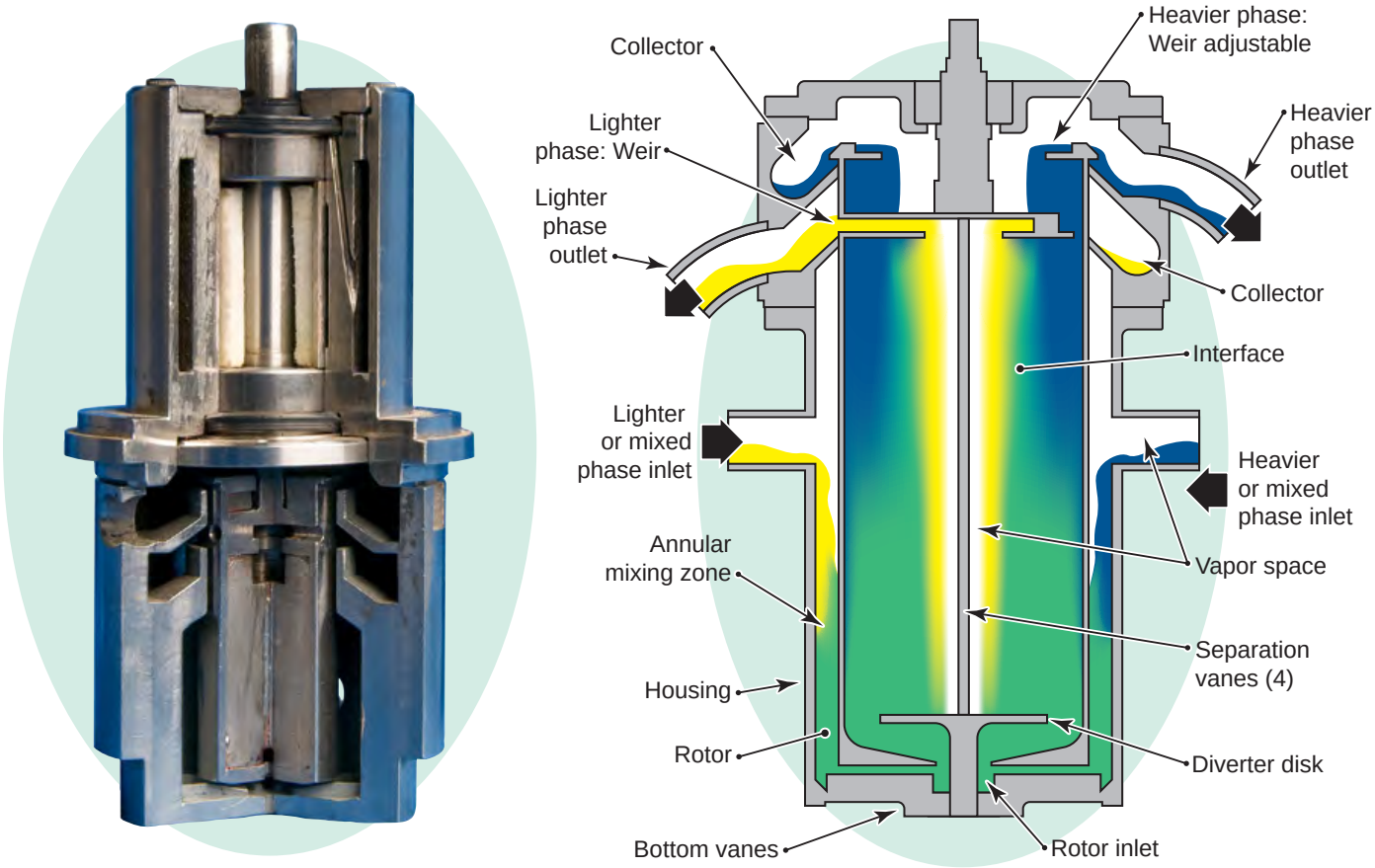


Figure 3. Cutaway of a development model (left) and cross-section schematic of centrifugal contactor (right).

extraction process is that cesium in the aqueous strip solution is concentrated in volume by a factor of about 12-15 compared to the feed solution, meaning a smaller volume to be processed in the DWPF. The solvent extraction process was developed by Dr. Bruce Moyer's team at ORNL, which helped SRNL deploy the chemistry for the complex SRS waste.

Centrifugal contactors are the heart of the equipment. Developed in the early 1960s, the contactors reduce the contact times and resultant solvent decomposition by effecting rapid separation of the phases using centrifugal forces. The SRS pioneered the use of centrifugal contactors in reprocessing of radioactive spent fuel and reactor targets. They have been successfully used at the site for over 40 years. Residence time in a contactor is short (about 10 seconds), minimizing radiation exposure. To obtain extraction efficiency, contactors are connected in series. In the MCU, seven contactors are needed in the extraction stages. Figure 3 shows cross-sectional views of a centrifugal contactor.

To develop and demonstrate the integrated processes, SRNL tested the chemistry with actual SRS samples at the composition extremes and performed continuous solvent extraction tests with smaller versions of the equipment in the MCU process. These tests successfully demonstrated the efficiency of radionuclide removal as well as volume reduction for the liquid requiring processing at DWPF.

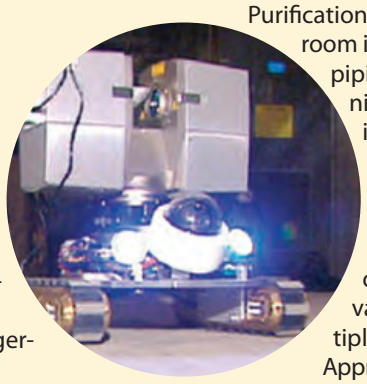
For example, small samples of actual HLW were tested in batches by contacting with the organic solvent system containing the BOBCalixC6 extractant and shaking. After separating, the two phases were sampled, and cesium concentration in each was measured. The cesium removal efficiency was calculated from these measurements. (A similar batch test was used to examine sorption behavior of MST and measure its removal efficiency for Pu, Sr, U and other actinides.)

The Decontamination Factor (DF) for a cesium extraction process is defined as the concentration of cesium in the feed divided by the concentration of cesium in the decontaminated stream. For the MCU, a DF greater than 12 is required.

When the full-scale SWPF is operational, a DF greater than 40,000 will typically be required. The lower DF for the MCU is

Technologies in the News

Remote-Control Laser System for D&D



The DOE complex nationwide has numerous facilities destined for deactivation and decommissioning (D&D), requiring characterization to support thorough work planning. Many of the facilities represent difficult challenges for adequate characterization because:

- High levels of contamination make it dangerous for employees to spend time inside,
- Structural deterioration makes it dangerous for employees to enter, or
- As-built engineering drawings do not exist or are unreliable.

To help meet that need, SRNL demonstrated a system that uses a remotely controlled laser scanning system to produce the high-quality engineering drawings needed to plan D&D activities of old, excess facilities, without putting human employees into harm's way.

Working with Savannah River Site's Area Closure Project, a commercially available laser scanning system was selected - GKS Inspection Services' FARO LS 880 - to meet the criteria for remote control, millimeter accuracy, and high scan speeds. This was paired with a remotely controlled deployment platform developed by SRNL from commercially available components.

The demonstration project, funded by DOE's Office of D&D and Facility Engineering, was conducted in the former Purification room in SRS' decommissioned P Reactor. The room is a moderate sized facility containing complex piping and valving systems that represent a significant, and realistic, challenge for the imaging system, as well as obstacles such as mobile stairways and scaffolds.

The deployment platform for the laser scanning system was operated remotely from another room in the facility. A video camera on board allowed the operator to navigate to various points within the room to provide multiple scanning angles for the laser system.

Approximately five hours of data was acquired from 20 locations in the facility. Laser image data sets produced point cloud images that were processed and loaded into a basic CAD package for further analysis.

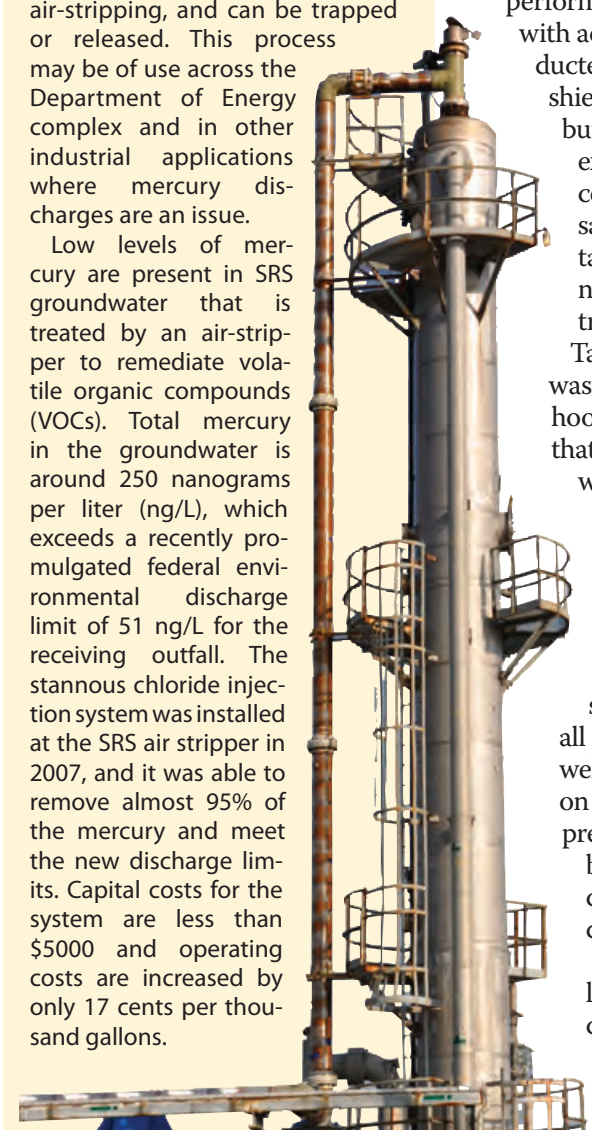
The imagery acquired during the demonstration project would be of great value for project planning. All piping systems were reasonably identified, including those in stacked/bundled configurations. Even with a very basic CAD system, the images could be manipulated to generate differing views of the room. Components could be selectively removed to provide better views of key structures. Dimensional data (length, surface area, volume) could be obtained for individual components. Between the on-board video and the real time laser acquisition, numerous potential obstacles (ladders, equipment, etc.) and suspicious materials could be identified in the facility. These data alone would allow refinement of the initial worker entry strategy.

Technologies in the News

Removing Mercury from Water Effluents

A technology idea developed under SRNL's R&D seed funding program has now been successfully deployed to remove mercury from one of the Savannah River Site's (SRS) outfalls. This simple, low cost technology involves the injection of stannous chloride, a reducing agent, to convert all the various species of mercury to elemental mercury. Elemental mercury is then removed from the water by air-stripping, and can be trapped or released. This process may be of use across the Department of Energy complex and in other industrial applications where mercury discharges are an issue.

Low levels of mercury are present in SRS groundwater that is treated by an air-stripper to remediate volatile organic compounds (VOCs). Total mercury in the groundwater is around 250 nanograms per liter (ng/L), which exceeds a recently promulgated federal environmental discharge limit of 51 ng/L for the receiving outfall. The stannous chloride injection system was installed at the SRS air stripper in 2007, and it was able to remove almost 95% of the mercury and meet the new discharge limits. Capital costs for the system are less than $5000 and operating costs are increased by only 17 cents per thousand gallons.



acceptable because it has a low activity feed and because an agreement with state regulatory agencies permits a higher activity for MCU's limited operational life to enhance technology for the SWPF operation.

The Chemistry Testing Program

Initial laboratory scale testing with simulated wastes occurred principally at ORNL with some work at ANL. SRNL resources concentrated on testing with radioactive waste samples. To develop the CSSX flowsheet before constructing the MCU, Dr. Walker and Dr. Bill Wilmarth performed a number of batch tests with actual SRS HLW. SRNL conducted these tests in the SRNL shielded cells to measure distribution values for composition extremes. Testing examined cesium mass transfer with samples from 11 of the 41 tanks containing supernate or salt cake that will be treated by these processes. Tank selection focused on wastes with the greatest likelihood to contain compositions that challenge the performance while covering the wide range of compositions expected during operations. For example, tanks with higher concentrations of organics that might interact with the solvent were examined. In all cases, performance agreed well with expectations based on simulant tests or with predictions from calculated behavior using an empirically-derived solvent model developed by ORNL.

The testing also established an upper feed concentration limit for potassium. Because BOBCalixC6 also binds potassium ions, high potassium concentration depresses cesium extraction and raises the susceptibility of the solvent to third-phase formation.

An important part of the CSSX flowsheet development was to process a large (10 gallons) blended sample of actual SRS solution using small (2cm diameter) contactors in the shielded cells. Dr. Walker, Dr. Norato and Bob Pierce led installation and testing of the equipment inside the shielded cells as shown in Figure 4. Testing showed a DF of 40,000, which meets the design objective for the large-scale facility. In addition, no third-phase formation occurred which could interfere with the extraction.

Larger-scale simulant testing at ANL showed relatively high solvent carryover in the aqueous phases, but more precise data were required to establish the droplet sizes. Dr. Fink and Dr. Charles Nash led SRNL efforts to confirm the expected concentration of entrained solvent and measure droplet sizes under a range of operating conditions using full-scale equipment and simulated waste. These results provided design data for enhancements in the flowsheet equipment with the addition of a coalescer (which promotes growth of solvent droplets to increase their buoyancy) and a decanter (which provides sufficient residence time for adequate separation of the organic and aqueous phases) for the strip effluent stream going to DWPF and for the decontaminated salt solution going to Saltstone.

Final MCU equipment fabrication and testing with simulated waste occurred at an industrial laboratory with the MCU equipment integrated into skids for placement in the facility. When commercial laboratories yielded unreliable results for tracking cesium in the mixed aqueous-organic samples, SRNL personnel completed those studies and verified the process met design objectives.

With the startup of MCU, Dr. Peters, Dr. Nash, Dr. Fernando Fondeur and Dr. Fink completed tests to verify process performance with the first two waste feeds. The efforts demonstrated performance that exceeds the design targets for the facility.

Solvent Analysis Development

The solvent for the CSSX process consists of the cesium extractant, BOBCalixC6, at 0.007 M concentration in a diluent, Isopar® L. The diluent is a branched aliphatic hydrocarbon with chemical and radiological stability that promotes good hydraulics for solvent extraction. A modifier, 1-(2,2,3,3-tetrafluoropropoxy)-3-(4-sec-butylphenoxy)-2-propanol (abbreviated Cs-7SB), is added at 0.75 M concentration to increase extractant solubility and cesium extraction. The fourth component is a suppressor, tri-n-octylamine (TOA), added to suppress deleterious impurity effects and to improve and stabilize stripping.

To support MCU testing, startup and operation, an analytical method was needed to monitor the four components in the solvent and to track any degradation. Dr. Tom White of SRNL developed several methods to monitor the four-component solvent. To support the process demonstration at SRNL, he developed a high pressure liquid chromatography method and a gas chromatography-mass spectrometry method. For routine operation of MCU, Dr. Steve Crump developed a simpler gas chromatography method with flame ionization detection. Dr. Fondeur developed numerous spectroscopic and thermal analysis methods to confirm solvent purity, monitor quality on process samples, and to assess safety issues for flammability control and organic stability in downstream facilities.

Online Cesium Analysis Equipment

SRNL was requested to develop online monitors to measure cesium concentrations in the two product streams – the decontaminated salt solution (<0.1 curies per gallon, Ci/gal) and the strip effluent (16.5 Ci/gal). This approach provides an early warning system should a process upset occur. Dr. Vito Casella and his team selected a gamma-ray monitor technique, which measures the gamma rays from the Ba-137m decay daughter in equilibrium with Cs-137.

The team installed redundant Geiger-Mueller tubes on the pipe leading to the strip acid effluent hold tank. This higher activity measurement was relatively straightforward. Figure 5 shows the

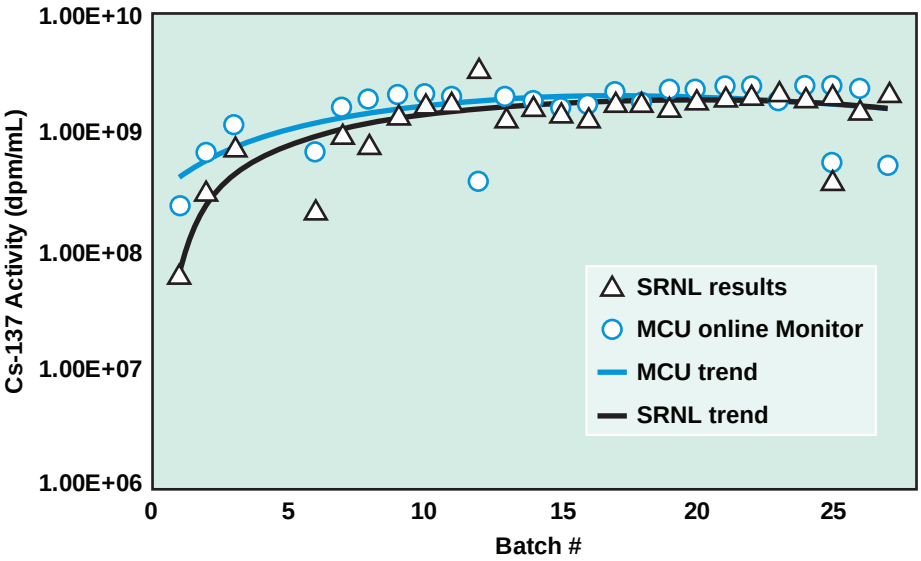


Figure 4 (top). Contactor equipment in Shielded Cell for tests with radioactive waste (yellow tint due to shielded cell window).

Figure 5 (bottom). Good agreement of in-line cesium monitor with samples analyzed at SRNL.

performance of the equipment versus strip acid samples collected and analyzed at SRNL.

For the lower sensitivity measurement on the decontaminated salt solution pipe, redundant thallium-doped sodium iodide detectors are installed. The required detection limit of 0.01Ci/gal in a high radiation background environment presented a challenge. Dr. Casella reduced the surrounding gamma radiation by designing a special tungsten alloy shield around the detector. The monitors successfully detect changes in cesium concentrations, allowing operators to verify proper operation of the process.

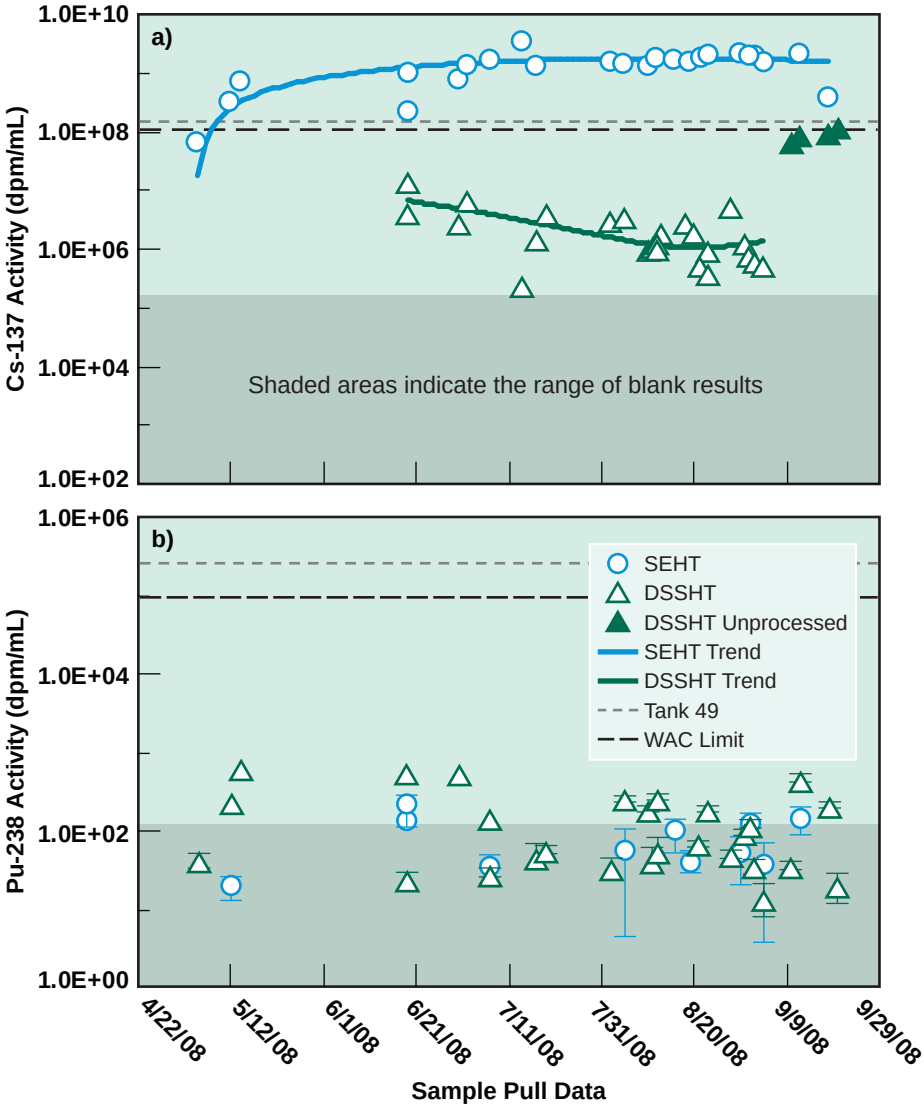


Photo (top). Extraction contractors installed in MCU.

Figure 6. (a) Cesium concentration in product streams during initial processing of radioactive waste. (b) Plutonium concentration in product streams during initial processing of radioactive waste.

SRNL Support for Initial Operations of MCU

Drs. Peters, Poirier, Fondeur and Fink provided support during the MCU preliminary trials, which used non-radioactive cesium in a simulated salt solution to test the equipment and process, and during the radioactive operations that followed.

The non-radioactive tests were successful, with DFs between 200 and 700 and concentration factors of 11-13 while treating aqueous solution at rates as high as 8.5 gpm. Also, the coalescer and decanter functioned very well with solvent concentrations less than the analytical reporting limit of 10 mg/L in the aqueous product streams.

Processing of radioactive waste began in April 2008, treating about 140,000 gallons of waste between April and September. Cesium and plutonium removal are shown in Figure 6. Cesium DFs reached a steady value over 100 with a concentration factor averaging 12. The slightly lower efficiency than observed in non-radioactive trials reflects the chemical composition of the more complex radioactive waste and not a decline in performance. For plutonium as well as for strontium, removal efficiencies significantly exceeded predictions from laboratory tests.

The Laboratory was able to help overcome a problem encountered during initial operations. The coalescer was clogging due to the precipitation of aluminum-bearing solids. SRNL analyzed fouled coalescer media from the facility and identified the species causing the problems.

In parallel to supporting ongoing operations, SRNL installed a prototypical full-size coalescer

and examined chemical cleaning approaches for recovering flow through fouled media. Chemical cleaning proved only minimally effective when conducted in the facility, and efforts shifted to designing a modification to install disposable filters in front of the coalescers to mitigate the fouling. Also, addition of extra caustic to the waste reduced the risk of aluminum precipitation. Those facility modifications and preparation of the second batch of waste for processing were completed, and operations resumed with the second large batch of waste.

Summary

Operation of the process to date has proven robust. While the processes are actively treating waste, their most important contribution is as a proving ground for the larger SWPF to come. Lessons learned in ARP and MCU operations are being incorporated into that upcoming facility. SRNL's technical focus is shifting toward opportunities to improve the chemical flowsheet. Of particular interest are enhancements that will allow the new facility to achieve even faster reduction in the SRS inventory of stored waste, bringing the Site ever closer to the day when all of its high-level waste has been treated and ready for final disposition.

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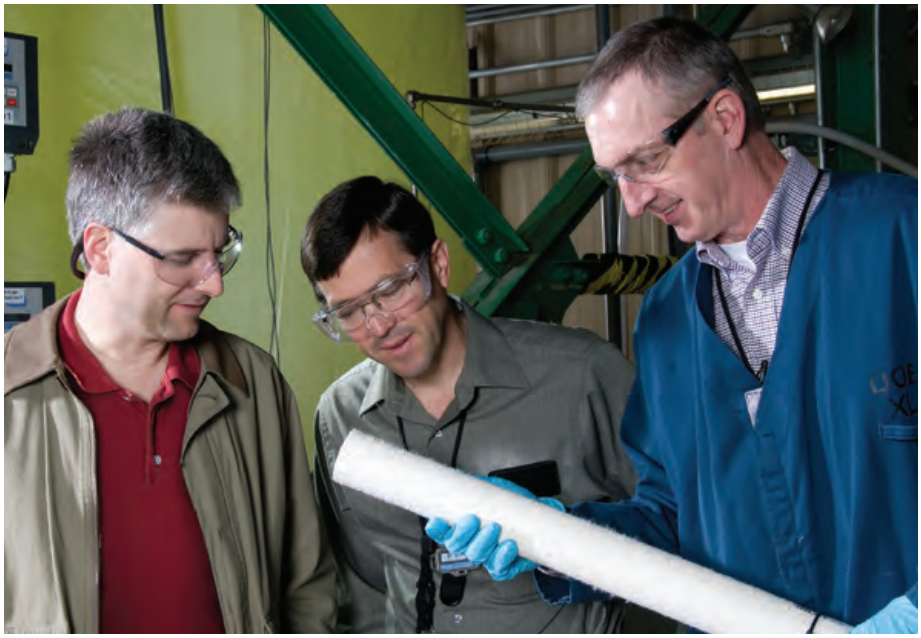


Photo (top). Dr. Tom Peters (left), Dr. Michael Poirier and Mark Fowley (right) examine disposable filters for use in the coalescers to mitigate fouling.

Photo (bottom). SRNL researchers Mark Fowley (left) and Dr. Michael Poirier (right) measuring pressure drop across various full-size coalescers to examine design changes to reduce clogging encountered in initial operations.

Advances in Mass Spectrometry Prepare NNSA for the Future

***SRNL led an initiative to ensure that an important analytical capability needed by the** National Nuclear Security Administration was maintained and even enhanced after equipment vendors announced that they were phasing out support for the crucial equipment. Highly precise instruments known as low mass, high resolution gas mass spectrometers are used at several NNSA sites across the country to measure gases used in production, surveillance and development activities related to the nation's nuclear defense. A few years ago, the manufacturers of these important instruments announced that they would no longer produce them and would cease support for them by 2013. With this initiative, SRNL redesigned electronic components of the existing equipment to extend its useful life, identified and modified other equipment as potential replacements, and is developing a new device that shows great promise as a replacement.*

You hate it when it happens to your home appliances: That trusty old device that has served you so well for so many years has been declared obsolete. The manufacturer no longer makes parts for it, doesn't have any service personnel who are trained to fix it, and plans to discontinue support entirely in just a few years.

It's inconvenient when it happens to your dishwasher. But often, the upcoming changes provide you an opportunity to gain an improved model with enhancements that make your life easier, and equip you for many years to come.

That's what happened to a class of instruments used by the National Nuclear Security Administration (NNSA). When manufacturers stopped making key instruments used to measure hydrogen and other gases used in production, surveillance and development activities related to the nation's nuclear defense activities, a team led by Savannah River National Laboratory stepped in. The result will carry the NNSA forward into the future.

The NNSA Nuclear Security Enterprise (NSE) provides the necessary support to maintain the safety, security, and reliability of the nation's nuclear weapons stockpile. Since the 1980s, the NSE has relied on low mass, high resolution gas mass spectrometry to measure the isotopes of hydrogen for product certification, surveillance, and development activities to support the nation's nuclear defense. In 2003, NNSA recognized it was at risk of losing this capability when the vendors who had originally provided the instruments declared these aging mass spectrometers obsolete, would no longer manufacture them, and would provide only minimal support until 2013, when support would cease completely.

SRNL, utilizing its years of expertise in adapting technologies for deployment in harsh, primarily radioactive, environments,

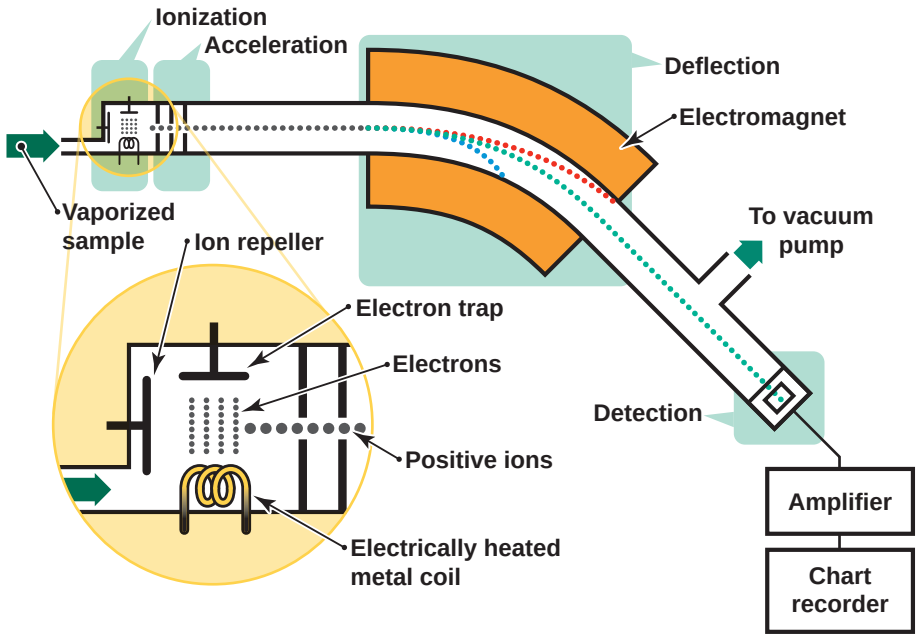
stepped up to lead the NNSA multi-site initiative to ensure that this extremely important analytical capability was maintained throughout the complex. Besides the Savannah River Site (SRS) Tritium Facilities, other Defense Program (DP) sites such as the Pantex plant in Amarillo, Texas; Y-12 Plant at Oak Ridge, Tennessee; Sandia National Laboratories; Los Alamos National Laboratory (LANL); Lawrence Livermore National Laboratory; and Pacific Northwest National Laboratory are stakeholders in this effort, with these facilities collectively owning approximately 20 instruments.

NNSA work with low atomic weight gases like hydrogen and helium places exacting requirements on these instruments. The mass spectrometers currently used at NNSA sites were specifically designed in the 1980s for this very challenging application.

They must be highly precise, accurate and sensitive. The instruments must be able to discriminate among the isotopes of hydrogen, protium (H), deuterium (D), and tritium (T); compounds that include the different hydrogen isotopes; and the helium isotopes. Mass spectrometers do this by segregating the various ions based on their mass to charge (M/Q) ratio.

Table 1 shows ions of interest in the mass 2-6 range and the instrument resolution required to discriminate among the ions. A lower-resolution instrument would not be able to distinguish among ^{4}He (M/Q ratio of 4.0026), HT (4.02388), and D_2 (4.028) ions. A reading from an instrument with a resolution of 975 would show three distinct peaks corresponding to ^{4}He, HT, and D_2 ions. The mass spectrometers currently used in the SRS tritum facilities are magnetic sector instruments that have a resolution of 3,000.

To guarantee the viability of the instruments used to measure tritium and associated low mass gases, SRNL initiated a multi-pronged strategy to: 1) redesign the electronic components and software of the existing mass spectrometers to extend their useful life, 2) identify modern, commercially available mass spectrometers that, with some modifications, could be potential replacements, and 3) evaluate alternative technologies to mass spectrometry for process control and monitoring. SRNL's goal was not to just maintain this capability but to enhance the data quality, instrument efficiency and productivity, and reduce the cost and instrument footprint where possible.



Ion (positive)	M/Q	Resolution (M/ΔM)
D	2.01400	1221 (D➔H_2)
H_2	2.01565	
^{3}He	3.01603	1580802 (^{3}He➔T)
T	3.01605	522 (T➔HD)
HD	3.02183	1831 (HD➔H_3)
H_3	3.02348	
^{4}He	4.00260	188 (^{4}He➔HT)
HT	4.02388	975 (HT➔D_2)
D_2	4.02800	
DT	5.03005	
T_2	6.03200	603 (T_2➔D_3)
D_3	6.04200	

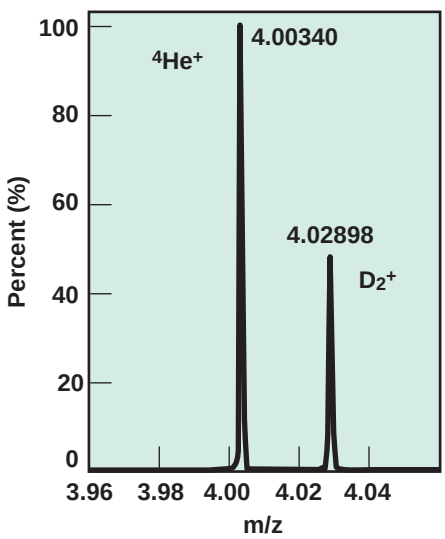
Figure 1 (top). Mass spectrometry basics. Clark, Jim (2000). [Diagrams of a mass spectrometer]. Chemguide: Helping you to understand Chemistry. Retrieved from http://www.chemguide.co.uk/analysis/masspec/howitworks.html

Table 1 (bottom). Important ions in the mass 2-6 range.

Opposite page. SRNL scientist Dr. Bill Spencer prepares to analyze a sample with the modified JEOL GCMATE high resolution mass spectrometer.

Principle of Mass Spectrometry

In magnetic sector mass spectrometry (Figure 1), the gas or vaporized sample enters an ionization chamber where the atoms or molecules are ionized by electrons from a heated filament. The positive ions are expelled from the ionization chamber through an aperture by an ion repeller. The ejected ions are accelerated and focused through several electrostatic collimating slits. They then enter an electromagnetic field where the ions are deflected and separated according to mass (M) and charge (Q). The lighter M/Q ions are deflected more than the heavier ones.



The system operates under a very high vacuum (<10-8 Torr) to eliminate air from the instrument and assure that the ions do not decay during their flight time. The ion intensity is measured versus the momentum of a given mass, as selected based on acceleration voltage and magnetic field strength. Sweeping either the accelerating energy or the magnetic field strength allows different ions to focus at a collector slit where ions are detected using a high gain amplifier to measure the collected charge. A plot of the ion intensity versus mass/charge ratio creates a mass spectrum like that shown in Figure 2.

Upgrading Existing Mass Spectrometers

A widely used vintage mass spectrometer in NNSA facilities which is currently at risk is the Finnigan MAT 271. This spectrometer was developed in the 1980s for a 10-lab group that included SRNL and SRS. These mass spectrometers are currently used at the SRS Tritium Facilities and at other DP sites. Access to the instruments used in SRS production facilities is virtually impossible because they are in constant use for process measurements, and all but one are contaminated with tritium, which is radioactive. In order to perform and test upgrades to the mass spectrometer, SRNL obtained a MAT 271 from Sandia National Laboratories. Under the interlaboratory agreement, the upgrades made by SRNL would then be available to Sandia as well as to the rest of the complex.

"We tried to use commercially-available modern components wherever possible," says Joe Cordaro, SRNL lead engineer for this program. "Still, a few high voltage components had to be custom-designed and built by us because none were available that met our demanding design requirements. This is a complete electronic overhaul of the instrument, starting from the source all the way to the detector, and includes power supplies, control systems and measurement systems."

Cordaro and his team had to custom-design and build the electrometer detector (also called a Faraday cup amplifier) and the emission regulator for the ion source. Custom, ultra-high resolution circuits were also designed to control the electric field. These, as well as all the purchased components, were tested after installation on the MAT 271. The results were very successful, with all the components meeting or exceeding their design requirements. For example, the new electronics provide the ability to take extremely small high voltage steps, which means that higher magnetic and electric field resolution can be achieved than on the mass spectrometers currently in use. However, the overall resolution of the instrument will still depend on the instrument's existing hardware such as the available slit widths. Using a two stage amplifier circuit versus the single stage circuit in the current instruments provides higher sensitivity.

The stability of the magnetic field in the instrument is far superior than in the current instruments, which results in more stable peaks and eliminates the need to retune or

Figure 2 (top). Ion intensity versus mass/charge ratio

Photo (bottom). Mass Spectrometry Development Team (l to r, George Reeves, Larry Feutral, John McIntosh, Don Varble, Joe Cordaro) with the MAT 271 development system.

mass calibrate the instrument as frequently. Labview software was incorporated into the instrument, which provides a higher level of automation and flexibility for the user. With the improvement in instrument stability and software, the efficiency of the instrument is increased, allowing a higher throughput of samples.

SRNL completed design and construction on the ion beam focusing chassis in 2009. The last remaining component to be designed and built by SRNL, the ionization source temperature regulator, is scheduled for the end of 2010. Once all the hardware upgrades are complete, the Analytical Laboratories at SRS will perform certification of the instrument.

As a result of the Finnigan MAT 271 upgrade, NNSA's Pantex plant contracted SRNL to upgrade two VG3038 Mass Spectrometers (similar instruments manufactured by a different vendor). After the first VG3038 was completed, Lorelei Woods, a scientist with B&W Pantex, said, "The technical staff from SRNL made several trips to Pantex to work with the scientists to ensure the upgrade covered everything required and to test their work as needed….We are very satisfied with the operation of the instrument. This upgrade will extend the life of the instruments for another 15 to 20 years." Pantex's acceptance testing of the first VG3038 showed that all acceptance criteria had been met. By December 2009, electronics upgrade of the second instrument had been completed, and startup testing begun.

SRNL is currently working with Sandia to upgrade their two MAT 271s. Other possible upgrades include MAT 271s at LANL and Pacific Northwest National Laboratory. There are about 20 mass spectrometers of this type in the complex.

"These new upgrades will not only extend the life of the mass spectrometers used by the Nuclear Security

Technologies in the News

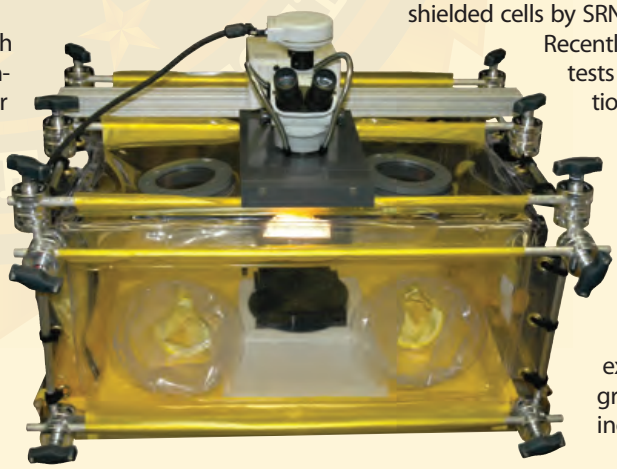
SRNL Develops Technology for Evidence Examinations for the FBI

With threats involving radioactive materials becoming more of a reality, SRNL is playing an important role for the Federal Bureau of Investigation (FBI) and the nation by providing facilities and the latest technologies to examine radioactively-contaminated evidentiary items. Since 2003, SRNL has been offering a valuable service to the FBI Laboratory. Technology had to be developed to facilitate the traditional forensic examination – which includes examination of DNA, hairs and fibers, latent prints, document forgeries, weapon ballistics, explosive residues and a wide variety of other materials – when that evidence is radioactively contaminated. To develop the needed technologies and techniques, the SRNL researchers interacted with the highly-trained Hazardous Evidentiary Analysis Team (HEAT) examiners from the FBI Laboratory.

SRNL has provided the Bureau with wet chemical decontamination methods to lower the radiation levels for safer handling without compromising the value of the evidentiary items. Decontamination processes are advantageous because they permit the hands-on physical examination of evidentiary items—a process that is often required of forensic examiners.

For radioactively-contaminated evidentiary items with low to moderate radiation doses, radiological containment, such as disposable PVC plastic glove bags and radiological hoods, provide safe handling. Disposable PVC containment is custom-made at the Savannah River Site, where it has a history of successful use in radiological work, and is routinely used to support various high-level waste operations, facility decontamination and decommissioning, and other operations. SRNL has developed a large variety of PVC glove bags and other containments to permit microscopy, photography, latent print enhancement, tool-marks and questioned document examinations with such items. These PVC containments prevent the need to conduct evidentiary examinations in radiological hoods, where strong ventilation drafts could be detrimental to some trace evidence forms containing hairs and fibers. They are also disposable.

Those items with high levels of contamination and/or radiation dose can be handled in radiological gloveboxes or in shielded cells, where highly radioactive materials are handled remotely by personnel positioned safely outside the cells. SRNL has developed disposable PVC liners for use in shielded cells, which have been demonstrated. These liners also help prevent evidentiary cross-contamination. Remotely-operated Raman and IR spectroscopic and latent print examinations have also been conducted in shielded cells by SRNL researchers and HEAT examiners. Recently, SRNL has conducted irradiation tests with materials that contain information of traditional forensic interest such as materials with latent prints.



In 2006, the FBI established the first phase of their radiological evidence analysis facilities at SRNL. In 2008, work began on the next phase. This new phase, to open in 2010, will greatly expand the Bureau's radiological evidence examination capabilities, taking even greater advantage of the close working relationship with SRNL.

Enterprise (NSE) by an additional 20 years, the upgrades will enhance the instruments' performance and efficiency, and will ensure a supply of spare parts and service," says Cordaro. "The help and encouragement we received from Sandia, Los Alamos and Pantex to take on this challenge has been essential to the success of this program. We've also had the excellent assistance of personnel from Analytical Laboratories and Tritium Maintenance Operations at the SRS Tritium Facilities."

SRNL's work on the MAT 271 upgrade also benefited DOE's Office of Environmental Management. In September 2009, SRNL used the MAT 271 upgrade design to complete an electronics and software upgrade of the Finnigan MAT 261 Thermal Ionization Mass Spectrometer used by SRS Analytical Laboratories to measure plutonium and uranium samples for SRS H Canyon and HB Line nuclear material stabilization programs. About 80 percent of the electronics used in the MAT 261 were used on the MAT 271.

Evaluation of Alternative New Instruments

In addition to upgrading the current instruments, SRNL undertook a parallel effort to identify commercially available instruments that, with some modifications, could complement or replace the mass spectrometers in the SRS Tritium Facilities and at other DP sites. A mass spectrometer that could meet the demanding requirements of the NSE applications did not exist, as determined from a survey of mass spectrometer manufacturers.

"We found the compact JEOL GCMATE to be the most promising instrument as a replacement for the mass spectrometers in the tritium facilities, if it could be modified to overcome some challenges" says Dr. Laura Tovo, SRNL lead scientist on this program. "We also found that the Quantra Fourier Transform-Ion Cyclotron Resonance (FT-ICR) instrument has phenomenal resolution – over 400,000 for mass 2 (the current Finnigan MAT mass spectrometers have a resolution of 3,000). With this high resolution, we can resolve all of the hydrogen isotopes and their compounds as well as many species in the mass 16-24 region that cannot be resolved and measured easily in a single scan with the existing instruments." Species with mass 16-24, such as water, ammonia, methane, and their counterparts composed of hydrogen's isotopes are unwanted impurities in the processing of tritium.

The resolution of the GCMATE is greater than 3,000 for masses 2-60, and the sensitivity meets the requirements for the SRS Tritium Facilities. However, as purchased, the instrument has complex ionization and detector options that are not useful for this application, and it has elastomeric o-ring seals that limit the vacuum and would not be compatible with radioactive tritium use. The SRNL team modified the instrument by simplifying the ion source and converting to metal gasket seals. All the modifications and upgrades were successfully completed, and the instrument met the resolution specifications (Figure 3), the hardest specification to meet.

The next steps in getting the GCMATE accepted as an alternative to the Finnigan mass spectrometers is to rigorously test it against the Finnigan MAT specifications and to develop tailored software for the tritium process environment. If it passes the Finnigan MAT specifications, then it will be installed in the tritium facilities and run in parallel to the current mass spectrometers for validation. Funding has been requested to complete this work in the next two years. The instrument

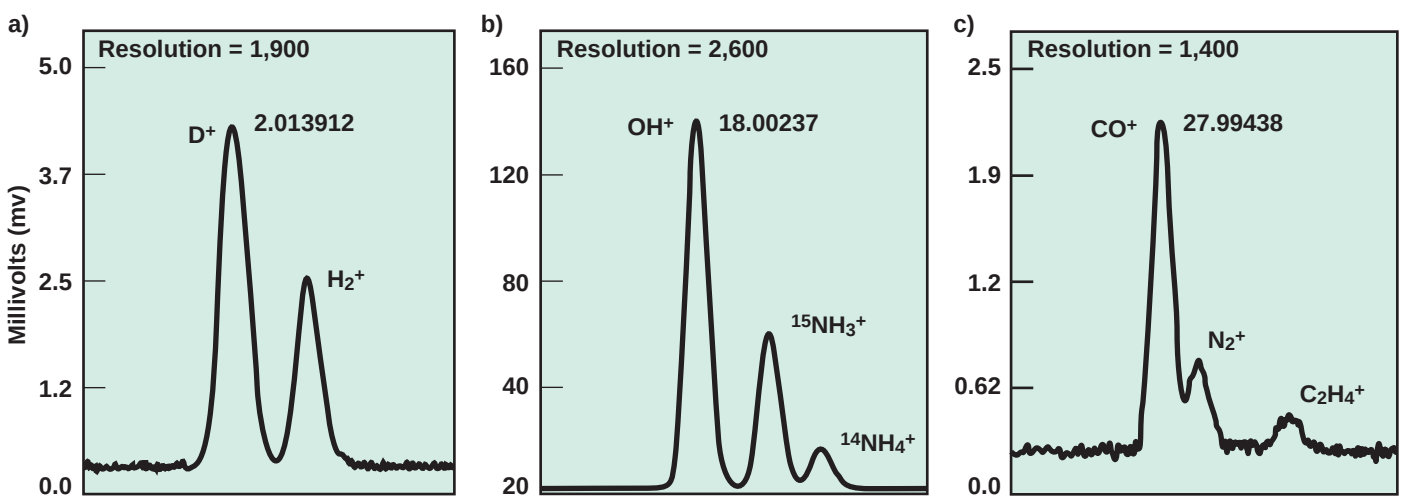


Figure 3. a) Trace hydrogen was detectable in a D_2 gas. H_2 was resolvable from the D^+ fraction that forms from the D_2 with resolution about 1,900. b) Shows the H_2O, $^{15}NH_3$, and $^{14}NH_4$ resolving at mass 18 with resolution 2,600. c) The GCMATE background at 1x $10E^{-8}$ Torr usually shows small traces of CO, N_2 and C_2H_4 at low ppm levels at masses 27.995, 28.006, and 28.03. A trace of H_20 and CO_2 were also usually detectable

might be further modified to allow use of traditional Faraday cup detectors and to take advantage of the new universal electrometer that was developed as part of the Finnigan MAT upgrades.

SRNL, LANL and Y-12 also worked with Siemens to modify their commercial Quantra FT-ICR for low mass analysis. Although the instrument does not meet all the performance specifications required as a replacement for the existing mass spectrometers, the re-engineered Quantra can provide a unique capability to the tritium facilities with its high resolution. For example, it can easily resolve CO and N_2, and the various isotopologues of methane, ammonia and water in a single scan. In order to be of even more benefit, its quantitative analysis capabilities must be improved by software and hardware upgrades. Additionally, performance testing in an environment that includes radioactive tritium must be completed before it can be put into routine operation.

New Instrument: Compact Crossed Fields Mass Spectrometer

Using Plant-Directed Research and Development (PDRD) funds from NNSA, Dr. Bill Spencer of SRNL is developing a new compact mass spectrometer for low mass isotopes. The instrument is potentially very low cost. The design is based on crossed electrostatic and magnetic fields to resolve the ions (Diaz and Gentry geometry).

The basis for this new device was the Mass Sensor R8 spectrometer. In order to obtain greater resolution, the ion radius was increased from 8 mm to 40 mm (Figure 4). The device uses a neodymium-iron-boron ($Nd_2Fe_{14}B$) permanent magnet, which fits in your hand. To design an optimal performing instrument, one must work at the ion focal points. Dr. Spencer uses a computer model (SIMION) to simulate and visualize the focal points of ions in the 2-40 mass range as shown in Figure 5. Currently, he is using a Burle ion imaging detector to simultaneously measure the focal points of multiple masses without scanning. The Burle detector uses a micro-channel plate (similar to an electron multiplier), a phosphor screen (to convert electrons to a visible image), and a digital camera.

"The next steps in the development of this compact mass spectrometer are to refine the instrument and to develop its quantitative capabilities," says Dr. Spencer. "I believe this instrument could be very useful as an in-line or in-process instrument. A number of NNSA sites may have uses for this instrument." Several invention disclosures related to this instrument have been filed by Dr. Spencer.

Summary

Through these projects, SRNL, in collaboration with other NNSA NSE sites, has ensured the viability of mass spectrometry to support the NNSA mission. The upgrades to modernize the existing mass spectrometers not only succeeded in increasing their useful life by at least 20 years but also enhanced the capability of the original instruments. Modification of commercially available mass spectrometers provides alternatives to the existing mass spectrometers at a lower cost and reduced footprint. Initial R&D efforts to perform high resolution mass spectrometry on-line look promising, and this work will continue with the goal of moving more analyses from the laboratory to the process line.

"Our NNSA customer has been very pleased with the progress we've made on several fronts to improve these critical instruments for measuring low mass gases," says Dr. Tovo. "We've secured the future of the production instruments and have made some new advances that will serve us well in the upcoming years."

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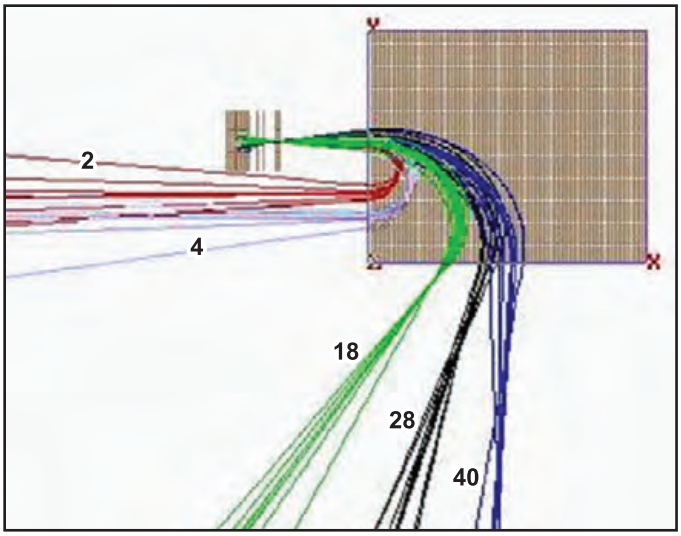


Figure 4 (top). Compact crossed fields mass spectrometer

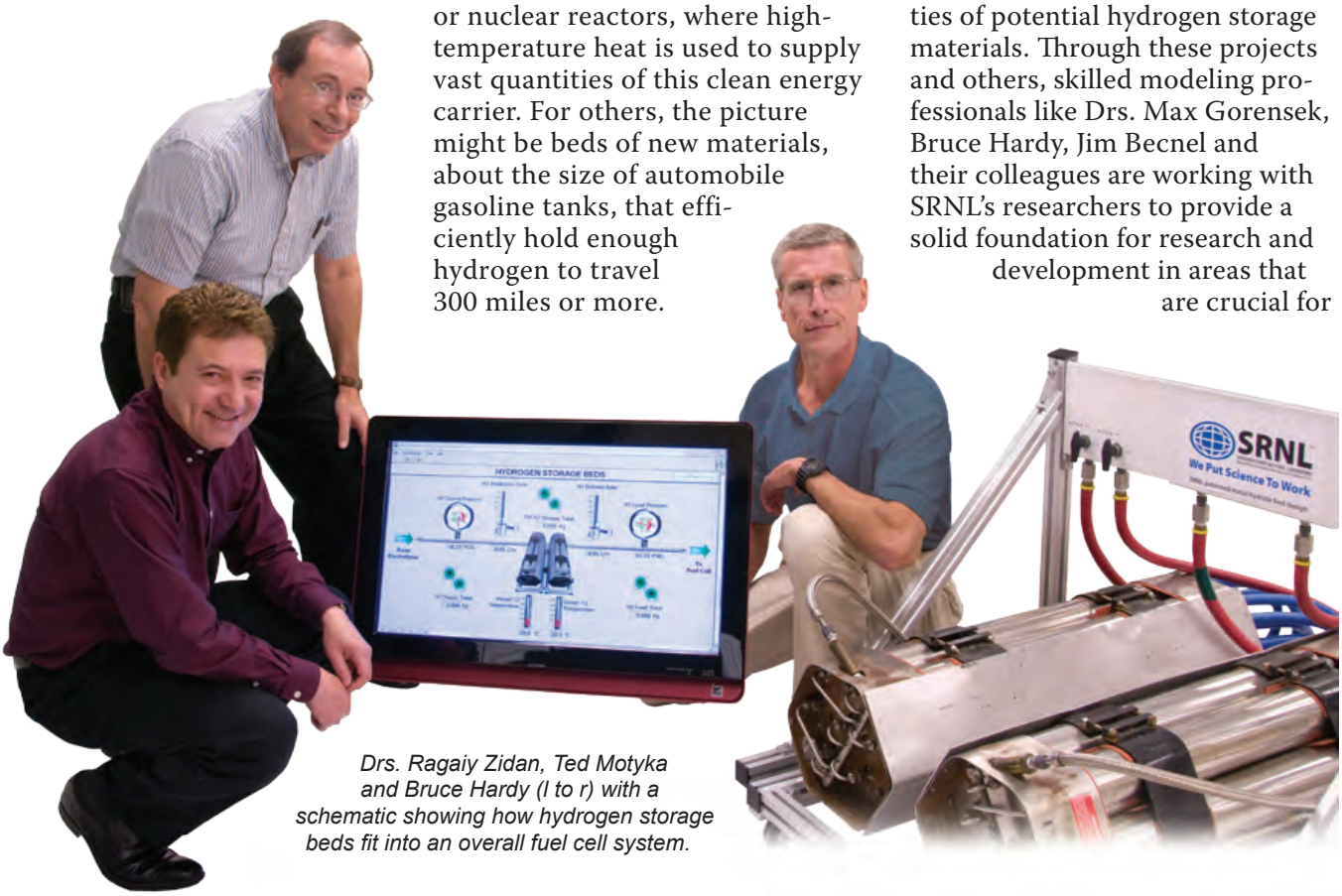
Figure 5 (bottom). Simulated ion beams using SIMION to model masses 2, 4, 18, 28, & 40

Modeling Our Energy Future:
Computational Science Applied to Development of Hydrogen Production, Storage and Distribution

***Developing new, efficient ways to produce, store and distribute hydrogen as a key part** of the nation's future energy strategy is the focus of a group of SRNL researchers. Providing a solid foundation for their experimental work are the Laboratory's modeling and computational science professionals. This group creates models that accurately predict the multiple aspects of complex processes, help the experimentalists understand the behavior of materials, and simulate system performance so components can be designed to work together effectively. These experts literally provide the vision of a hydrogen economy.*

Picture a new "hydrogen economy," and the image that may come to mind is a town full of industries and homes where hydrogen supplies power needs without creating greenhouse gases or other pollutants. For some researchers at SRNL, it may bring to mind large solar furnaces or nuclear reactors, where high-temperature heat is used to supply vast quantities of this clean energy carrier. For others, the picture might be beds of new materials, about the size of automobile gasoline tanks, that efficiently hold enough hydrogen to travel 300 miles or more.

For SRNL's modeling and computational science personnel, however, the images are more immediate and already exist. They range from engineering-scale process models for optimizing performance of hydrogen production systems, to atomic-scale models for exploring fundamental properties of potential hydrogen storage materials. Through these projects and others, skilled modeling professionals like Drs. Max Gorensek, Bruce Hardy, Jim Becnel and their colleagues are working with SRNL's researchers to provide a solid foundation for research and development in areas that are crucial for



Drs. Ragaiy Zidan, Ted Motyka and Bruce Hardy (l to r) with a schematic showing how hydrogen storage beds fit into an overall fuel cell system.

a future hydrogen economy – areas like hydrogen production, storage and distribution.

Hydrogen Production

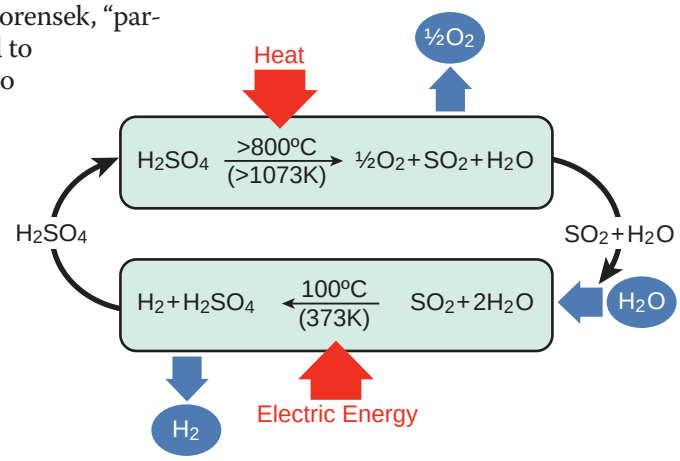
While hydrogen is one of the most plentiful elements on earth, nearly all of it is chemically bound in compounds such as water, hydrocarbons, and carbohydrates. Substantial energy must be invested to produce pure hydrogen. "Fortunately, one very efficient way of addressing these energy requirements is by nuclear energy," says Dr. Bill Summers, who leads SRNL's hydrogen production programs. "When nuclear energy is combined with a thermochemical water-splitting process, it can produce large quantities of hydrogen with minimal impact on the environment."

SRNL is leading development of the Hybrid Sulfur (HyS) process, a promising thermochemically-based method for using high temperature heat from advanced reactors or solar furnaces to split water into hydrogen and oxygen. The HyS process uses sulfur dioxide (SO_2) to depolarize the anode of an electrolyzer, reducing the electric power needed to make H_2 by over two-thirds when compared to water electrolysis. This causes sulfuric acid (H_2SO_4), instead of oxygen, to form at the anode. High temperature catalytic decomposition of the H_2SO_4 regenerates the SO_2 (which continues to recycle through the system), and produces a high purity O_2 co-product. These main steps of the HyS process are illustrated in Figure 1.

The total energy input for the HyS process is largely governed by these two reaction steps. The thermochemical step requires input of high temperature heat, while the electrochemical step requires input of electricity. The efficiency of the overall HyS process is optimized by balancing these two energy inputs.

In support of these activities, SRNL has the lead in developing a sulfur dioxide-depolarized electrolyzer (SDE) that employs proton exchange membrane (PEM) technology to efficiently produce H_2 from SO_2 and H_2O. To assist in this goal, SRNL's Dr. Gorensek developed a model to provide accurate predictions of SO_2 solubility in the H_2SO_4 anolyte, allowing the determination of reversible cell potentials; the lower the reversible cell potential, the less electricity is needed per mass of hydrogen produced. Dr. Gorensek used existing models in novel combinations to establish the effects of pressure, temperature, and acid concentration in this highly complex and difficult-to-model system. "The results were surprising in some respects," says Dr. Gorensek, "particularly with regard to pressure. Contrary to expectations before the start of the modeling effort, simply increasing the pressure as high as possible does not yield optimal SDE performance." At low pressures, the low solubility of SO_2 in H_2SO_4 does require higher pressures to be used to reduce the cell potential to an efficient range. However, as pressure is increased, SO_2 reaches a solubility limit, and further pressure increases serve only to increase hydrogen pressure at the cathode, which actually increases the cell potential. This optimization is illustrated in Figure 2.

This computational result has had a profound impact on SDE design and the development of the HyS process as a whole. The SDE model is also being used to describe the theoretical maximum performance of the SDE; this model is used in conjunction with mass transfer models to provide



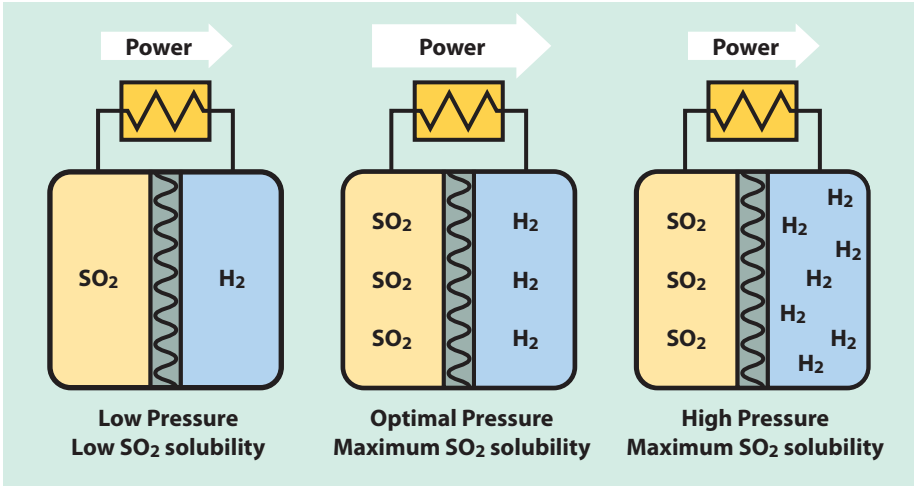


Figure 1 (top). Main steps in the HyS process.

Figure 2 (bottom). Illustration of the optimum of power output with increasing SDE pressure discovered using the system model. The power output is inversely proportional to the cell potential, which is affected by both the SO_2 solubility and the H_2 partial pressure.

guidance to equipment development efforts seeking to maximize SDE equipment performance.

Computational methods at SRNL have also been used to establish the performance envelope of the Sandia-developed bayonet reactor for the H_2SO_4 decomposition reaction. This reactor uses a tube-in-tube design to expose the sulfuric acid to high temperatures necessary for the decomposition. The sulfuric acid enters an outer tube and passes over a hot catalyst, which results in decomposition products that are then withdrawn through the inner tube, which supplies a recuperative heating effect. SRNL has modeled this reactor configuration to determine its high temperature heat requirements, without need for a detailed heat transfer analysis. The minimum high-heat requirement is obtained from a thermodynamic "pinch analysis" based on reactor model simulations.

Since the high-temperature heat requirement and SDE cell potential are major factors in determining the feasibility of the HyS process, these SRNL models are being used to identify the optimum process conditions, which can vary based on flowsheet conditions. These optimal conditions are then used in the design basis for experimental and prototype designs. The optimum conditions for the reactor and the SDE, however, cannot be taken independently from the HyS process. To optimize the production of hydrogen from water, a complete process flowsheet model is needed.

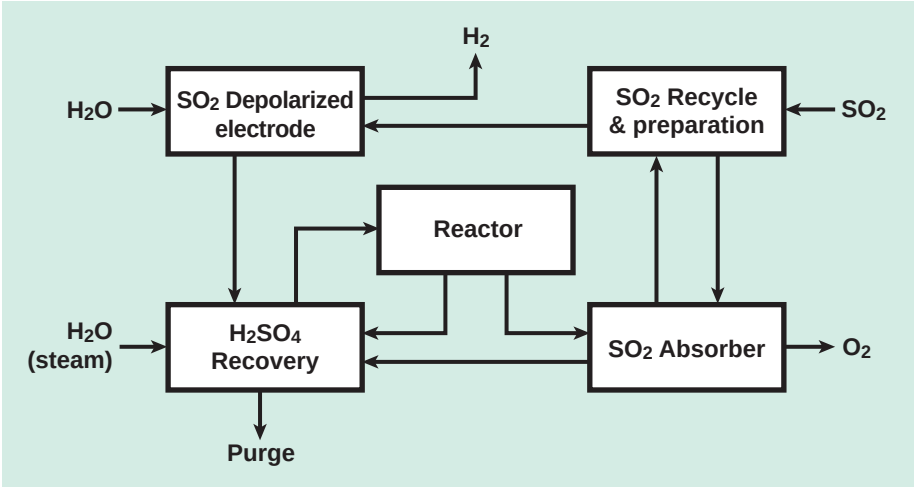


Figure 3 (top). Simplified flowsheet of the HyS process showing major processes and their connectivity.

Photo (bottom). Drs. Max Gorensek (right) and Bill Summers examine data from the control system used in the SDE development apparatus; data is directly compared to model simulations to help direct the development effort and refine model accuracy.

Development of a HyS process flowsheet that covers all of the elements of the process – including the bayonet reactor, SDE, SO_2 scrubber, sulfuric acid recuperation, and associated recycle processes (Figure 3) – requires a flowsheet model that provides accurate phase equilibrium predictions for the H_2SO_4-H_2O-SO_3-SO_2-O_2 system. The available "off-the-shelf" models have significant issues, including temperature range limitations and incomplete solubility data. Dr. Gorensek started with the existing models, but improved upon them by including SO_2 solubility in highly concentrated H_2SO and developing a simulation that can switch between the applicable phase equilibrium models as appropriate.

Detailed simulations of the complete HyS flowsheet allow an economic analysis of the HyS process as compared to other available technologies. This guides research and development by determining minimum efficiency needs and providing the theoretical maximum efficiency for each step in the process. Development can then focus on those aspects of the process that show the greatest potential for efficiency gains.

Hydrogen Storage

Once hydrogen is produced, it must be distributed and stored to be available on demand. Hydrogen storage research at SRNL includes new material development and potential use of these materials in both stationary and mobile

hydrogen storage systems. "We rely on the work of our experts in computational chemistry, unit operation modeling, and process modeling for information that helps direct and support programmatic goals," says Dr. Ted Motyka, who leads SRNL's hydrogen storage programs.

First principle modeling has been helping experimentalists to understand fundamental mechanisms of the formation and decomposition of hydrogen storage materials, and to validate the occurrence of intermediates. For example, a fundamental study to understand nanoscale level of hydrogen sorption behavior of carbon nanostructures, being conducted by SRNL's Dr. Ragaiy Zidan in partnership with Virginia Commonwealth University and University of Uppsala in Sweden, is closely linked to relevant modeling studies of these materials. Advances in hydrogen storage technology based on carbon nanostructures require the development of a basic understanding of their physicochemical properties and the manner in which these properties influence the hydrogen bonding. The team's effort is focused on understanding the hydrogen interaction mechanisms such as physisorption, weak covalent bonding, and chemisorption in these nano-carbon systems. The electron affinities were calculated for various carbon

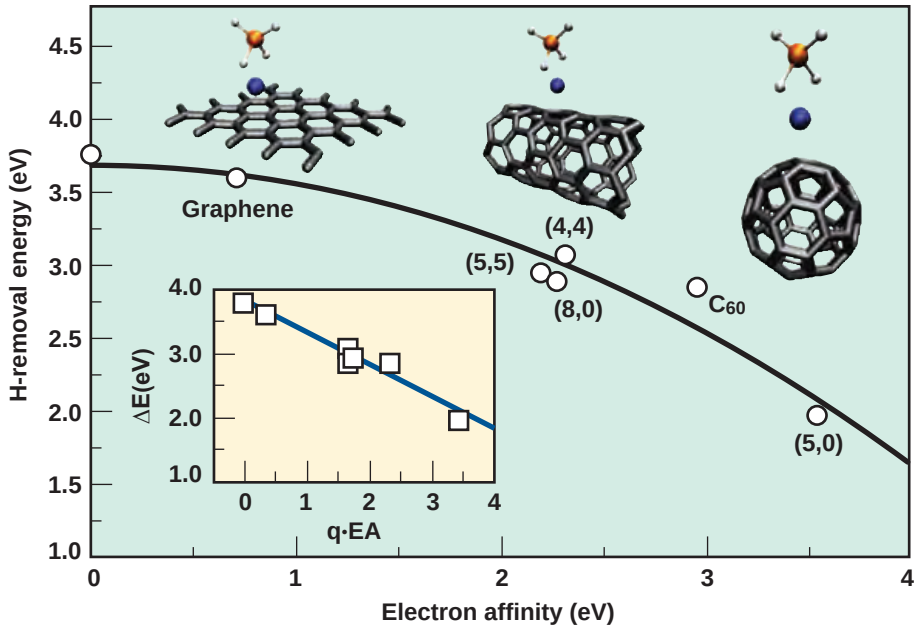


Figure 4. The electron affinity is found to depend upon the curvature of the substrate, and it increases with increasing curvature. The fullerene material, C_{60}, has a diameter of 7 Å with increased curvature relative to the 8-50 nm diameter multi-wall carbon nanotubes used in the experiments, indirectly resulting in its strong relative catalytic activity.

Technologies in the News

SRNL Supports Fuel Cycle Technology

The Savannah River National Laboratory (SRNL) is one of ten National Laboratories involved in Research and Development (R&D) for the U. S. Department of Energy's Fuel Cycle Research and Development (FCR&D).

The fundamental goal of FCR&D is to close the reactor fuel cycle and help move the United States away from its current once-through strategy. SRNL is a natural fit for FCR&D due its long history of R&D support to the separations processes used at SRS over the past 50 years and the waste solidification processes that are immobilizing SRS waste.

To minimize the waste being sent to a final repository and to recycle uranium for fuels, FCR&D is developing science-based separations processes. Analogous to a household waste recycling center, these processes would take civilian nuclear reactor fuel and chop/dissolve/separate it into zircaloy hulls, uranium, tritium, krypton, fission product and actinide streams. The uranium would be recycled into fresh reactor fuel, the actinides would be transmuted into shorter-lived radionuclides in a sodium-cooled Advanced Burner Reactor, and the volume of waste ultimately going to the repository would be less than today's single-pass approach.

Based on SRNL's process expertise, SRNL has performed fuel chopper studies, acid recovery system evaluations, plant simulation modeling. Building off SRNL's demonstrated competence with melt-dilute, DWPF, and fluidized-bed mineralization; SRNL has developed metallic, glass, and mineralized waste forms.

Several FCR&D processes have been successfully demonstrated in SRNL's shielded cells (shown), which provide a unique capability to safely perform work with highly radioactive samples.

Hydride	Experimental ΔH_f (kJ/mol)	Literature DFT ΔH_f (kJ/mol)	SRNL DFT ΔH_f (kJ/mol)
VH_2	-32	-66	-67
NaH	-57	-43	-42
KH	-58	-41	-47
MgH_2	-75	-64	-61
LiH	-116	-87	-84
TiH_2	136	-152	-150
BaH_2	-172	-144	-154
SrH_2	-176	-168	-167
CaH_2	-188	-172	-174
ScH_2	-201	-200	-205
LaH_2	-208	-190	-178
YH_2	-228	-210	-217
$NaAlH_4$	-115	-116	-101
$LiAlH_4$	-119	-113	-106
$NaBH_4$	-191	-198	-150
$LiBH_4$	-194	-180	-218

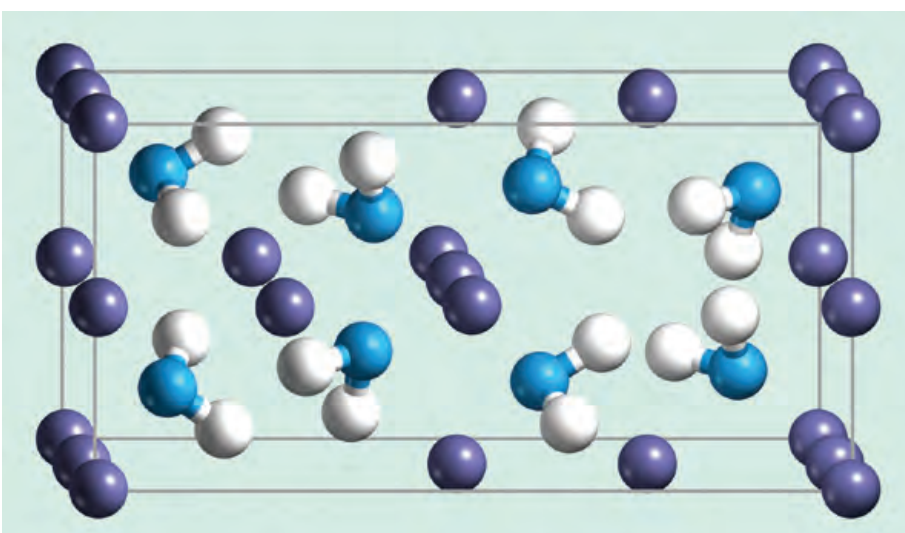


Table 1 (top). Tabulated values of ΔHf for hydride materials.

Figure 5 (bottom). The atomic structure of $LiNH_2$ shows its high hydrogen storage capacity; based soley on its structural information, computational chemistry can predict identification signatures (like XRD) as well as the effect of atomic-level changes in the relative strength of hydrogen bonding.

nanostructures to determine the origin of and energy difference for the hydrogen removal from supported NaAlH4 as shown in Figure 4.

Similarly, SRNL uses computational chemistry to predict the long-term stability of combinations of various materials. One method used in developing new hydrogen storage systems is to combine materials with known storage properties in order to develop new composites with improved properties. Although this process is conceptually simple, the ability to predict the long-term stability and performance of these new combinations is a formidable challenge.

One SRNL study, led by Dr. Don Anton, compared the heats of formation of compounds used in hydrogen storage material development; a sample is shown in Table 1. As seen in the table, the work provided a good relative stability comparison to that available in the literature, and good agreement was also shown with similar Density Functional Theory (DFT) calculations present in the peer-reviewed literature.

By studying the relative stability of various hydride materials, researchers can gain an understanding of material performance as defined by atomic-scale phenomena. This knowledge can be used to select new material combinations and material targets for development.

Additionally, stability analysis can help elucidate hydrogen storage mechanisms. For instance, the hydration of $Li_2Mg(NH_2)$ produces $Mg(NH_2)_2$ and LiH. However, stability analysis of possible products of $Li_2Mg(NH_2)$ hydration shows that two stable materials, $LiNH_2$ and Mg_3N_2, will form if there is insufficient hydrogen to completely form the $Mg(NH_2)_2$ product. In this case, the stability analysis helps confirm the presence of and identify reaction intermediates.

Computational modeling is also used to identify new and improved materials, compositions and systems. By definition, novel materials will not have verified analytical signatures such as diffraction patterns, IR spectra, and Raman spectra. When confronted with an unrecognized signature, computational chemistry can provide signatures of novel compounds as well as mixtures of compounds. In the cases where sufficient information is available, Monte Carlo methods are employed to reverse-fit the structure.

As an example, $LiNH_2$ is an important material for hydrogen storage due to its high capacity for hydrogen, but the hydrogen is too strongly bound to allow release at targeted operating temperatures. Due to various structural properties, it is an ideal candidate for alloying studies aimed at novel compound production, and such augmentation may produce a viable storage compound. As an example of providing analytical signatures, computational tools have been used to predict the neutron diffraction pattern of the deuterated form of $LiNH_2$ directly from its crystal structure. The crystal structure is shown in Figure 5 and the calculated neutron diffraction trace agrees with the experimental trace with an Rwp (weighted residual factor) of less than 6%. By demonstrating successful identification of known compounds, SRNL researchers can validate the presence of new structures by eliminating the known possibilities.

The material used for hydrogen storage must ultimately be confined in a system that can both supply hydrogen on demand and be rapidly refueled with hydrogen.

Dr. Hardy has developed a Metal Hydride Storage Tank (MHST) model that couples the conservation of mass, momentum, and energy with chemical reactions to provide a complete picture of storage performance. Using this finite-element model, detailed transient calculations can be performed on various storage tank designs. A transient analysis of temperatures for a fin-and-tube storage tank (shown in the Figure 6) shows the temperature distribution in a metal hydride storage bed as it is being refueled. The SRNL-developed model accounts for flow of the hydrogen within the storage material, the chemical process of hydrogen uptake, heat transfer by both mass transport of hydrogen, and conduction through the particles and fins. "By analyzing the various proposed storage modifications, the model not only provides the overall heat transfer characteristics, but can illustrate what limitations exist in any particular approach," says Dr. Hardy.

One of the many uses of this model is to identify necessary properties for storage media to meet technical targets. Most current material development guidance is based on the properties of microscopic crystals, such as hydrogen uptake rates, gravimetric density, and reversible quantities of hydrogen storage. These properties do not necessarily address the criteria of a successful hydrogen storage system at the engineering scale. For example, one important refueling limitation is the macroscopic heat transfer rates of the storage material, which is a quantity rarely explored during material development efforts. Models like the MHST provide guidance on the practical needs and limitations of hydrogen storage materials.

Hydrogen Delivery

The end result of the hydrogen fuel cycle is the delivery of energy to perform work. An obvious example of this is a hydrogen–powered vehicle. The delivery of hydrogen allows for the use of a fuel cell, which produces energy more efficiently than an internal combustion engine. The electrical energy produced by the fuel cell can directly power electric motors to move the vehicle. To examine the performance of such a fuel cell engine, SRNL's Mark Jones has coupled the various unit models into a simulation of a 75 kW fuel cell, which is illustrated in Figure 7. This simulation balances flows of materials and energy, integrating the mobile hydrogen storage system with the fuel cell, cooling system, and ambient conditions. This hydrogen-powered engine model provides operating capacities, given the various specifications for each individual component. This helps

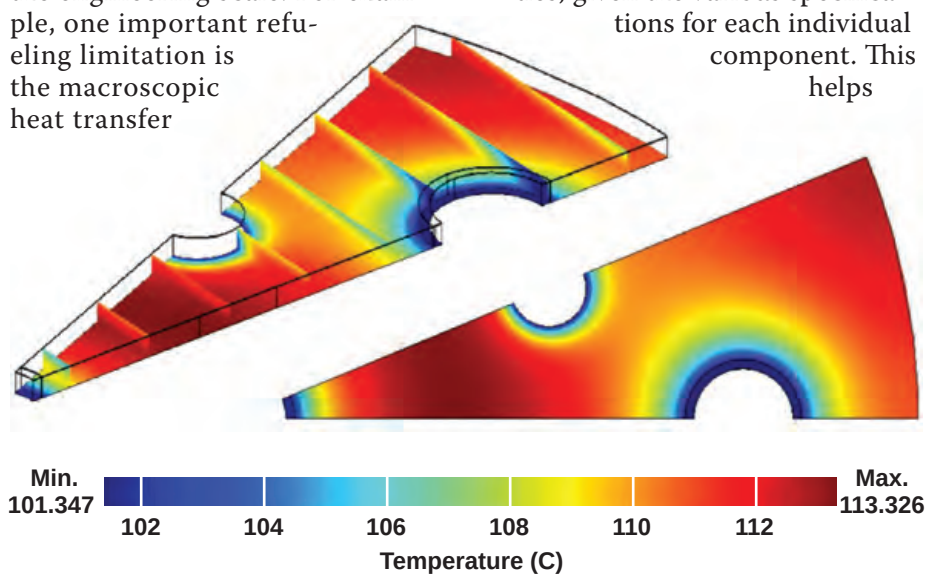


Figure 6. Illustration of temperature profile within a model fin-and-tube metal hydride storage tank during the refueling of hydrogen.

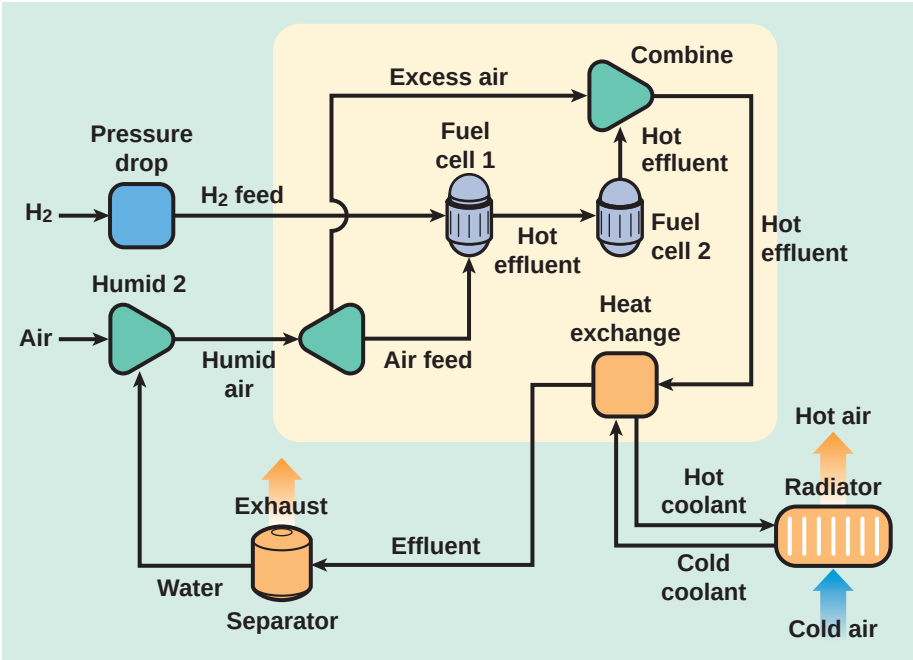
assure that individual component design targets are consistent with other components and, if met, will combine to deliver a system that provides the proper operating characteristics. Using this simulation, researchers are able to quantify the design needs of such a vehicle, including required heating and cooling loads at given power outputs. Similarly, effects such as fuel cell dehumidification can be studied as functions of ambient conditions and power consumption.

This work is focused on providing the dynamic balance between the operating conditions needed for fuel cells and the DOE-targeted hydrogen storage method performance.

SRNL is also using computational modeling to examine hydrogen distribution. In a future of hydrogen-powered vehicles, a hydrogen delivery infrastructure is essential to support on-demand refueling. One approach is a centralized hydrogen production facility that is connected to hydrogen filling stations by pipeline (similar to natural gas distribution) or by delivery trucks (similar to gasoline distribution), while another is a distributed system based on numerous regional and local hydrogen generating systems, including systems located in our homes. Most distribution models include the hydrogen analog of the conventional gas station.

Jones has developed a computational model of a hydrogen refueling station to examine its operating characteristics. The most important consideration of such a facility, as it turns out, is the heat load during fueling and the required cooling capacity. The SRNL model employs a "typical" hydrogen refueling station based on DOE targets and existing gasoline filling station operations. The purpose of this design is to determine typical heat loads, how these heat loads will be handled, and approximate equipment sizes.

Initial computational results indicate refueling stations (Figure 8) may be limited by the number of cooling towers needed to dissipate the large amount of low-grade heat that evolves during the rehydrogenation of current generation hydrogen storage materials. Assuming a generic hydride with a heat of formation of 27.5kJ/mol (exothermic), significant amounts of energy are released in the form of heat during refueling. For a moderate sized filling station of 8 pumps (16 refueling points), peak fuel demand would be approximately 480 kg H_2 / hr, which requires 6.5 GJ of heat dissipation.



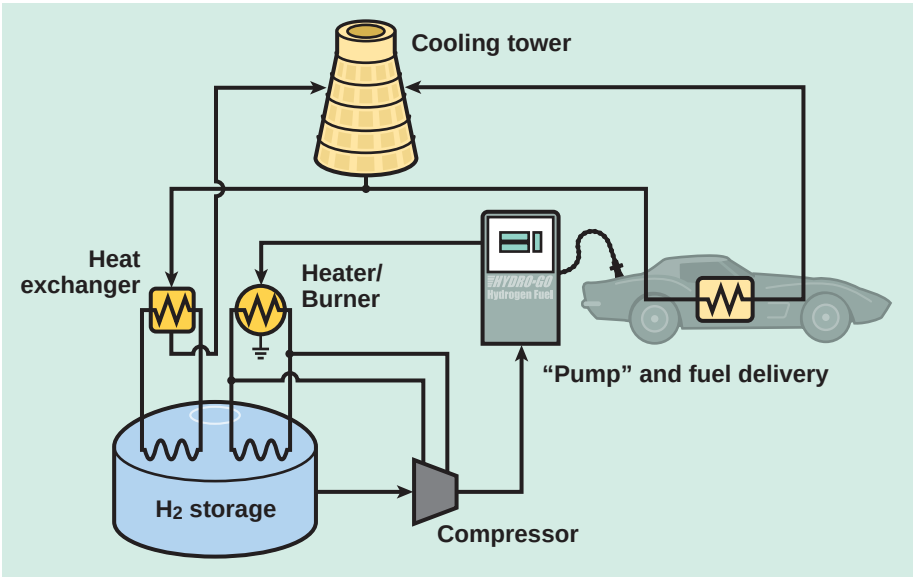


Figure 7 (top). Block diagram of the 75kW fuel cell engine process model, which integrates mass and energy balances for all important steps, including cooling system, humidifier, and fuel cell stack.

Figure 8 (bottom). Illustration of a model refueling station that employs the same metal hydride in its storage tanks as in the on-board vehicle storage.

Assuming the same hydride material is used in the fueling station as in the vehicles, the heat cannot be recuperated and must be dissipated to the environment; cooling towers provide the only efficient means of cooling this large amount of energy. For the moderate sized fueling station, this load would require a 500 ton cooling tower, which is approximately 18' tall with a 20' by 22' footprint. Large, interstate fueling stations might have 24 pumps or more, implying that such a station would require at least three 500-ton cooling towers, taking a footprint of approximately 20' by 66'. Clearly, the DOE-specified hydrogen storage material targets must be balanced not only for the vehicles, but for the fueling stations. And the fueling stations must balance their storage targets with the hydrogen distribution system.

Summary

Computational science and modeling continue to provide support to a variety of SRNL researchers and programs in areas of hydrogen production, storage and distribution. Ongoing work focuses on improving the accuracy of models that predict key material properties, expanding capabilities in developing the compositions of structures of dilute or amorphous systems, and in providing dynamic versions of fuel stations and hydrogen based vehicles of the future.

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Technologies in the News

Collaboration Examines Offshore Wind Potential

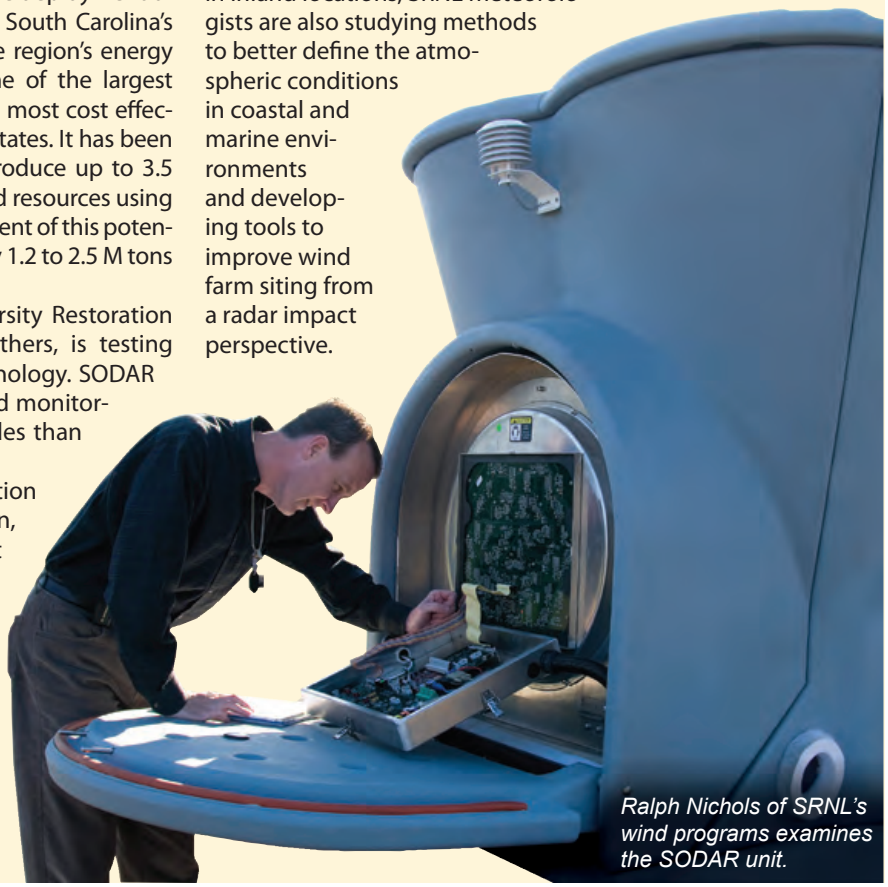
The Savannah River National Laboratory (SRNL) and its partners are testing, developing and evaluating new technology for assessing the coastal and offshore wind potential of coastal South Carolina counties. The ultimate goal is the deployment of offshore wind energy technology to diversify South Carolina's energy portfolio and significantly increase the region's energy independence. The Eastern seaboard has one of the largest untapped supplies of wind energy (one of the most cost effective renewable energy sources) in the United States. It has been estimated that South Carolina alone could produce up to 3.5 GW of power from its coastal and offshore wind resources using existing technology. Capturing less than 3 percent of this potential would reduce greenhouse gas emissions by 1.2 to 2.5 M tons per year and up to 16K tons of SO_2 emissions.

The partnership, including Clemson University Restoration Institute, Coastal Carolina University and others, is testing Sound Detection and Ranging (SODAR) technology. SODAR has the potential to provide high fidelity wind monitoring at a significantly greater range of altitudes than traditional meteorological towers.

Testing of SecondWind's Triton SODAR station was initiated on an island near Georgetown, S.C., then moved to an offshore U.S. Coast Guard platform in August 2010. The offshore testing will study the compatibility of the Triton SODAR in ocean conditions, develop algorithms to correct for movement caused by ocean waves, and study the impact of the ocean's acoustic environment. Data will be collected from the platform for one year to better understand the wind characteristics along the transitional area from offshore to the coast.

As part of this project, the partners also installed small wind turbines at five high schools, and at the Center for Hydrogen Research in Aiken, S.C., where much of SRNL's energy research and development is located. They are intended as permanent installations to educate communities about wind power, and understand their concerns regarding its use.

Because the conditions that affect wind farms' impact on radar are very different near the nation's shores than in inland locations, SRNL meteorologists are also studying methods to better define the atmospheric conditions in coastal and marine environments and developing tools to improve wind farm siting from a radar impact perspective.

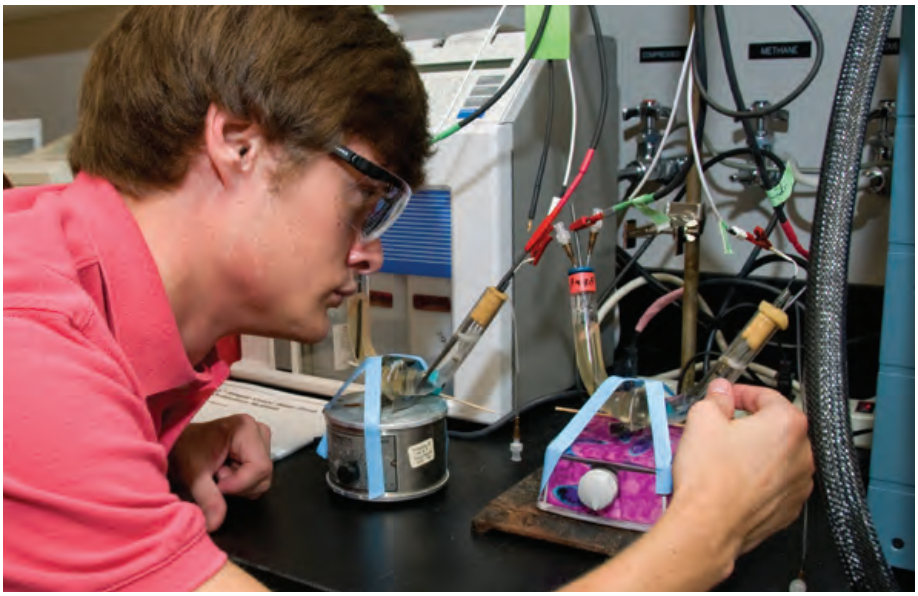


Ralph Nichols of SRNL's wind programs examines the SODAR unit.

SRNL Interns Gain Valuable Research Experience

For one group of students, summertime meant time to head into the laboratory, *the reading room or out into the field, to contribute to research projects that support the nation's national and homeland security, energy security, or environmental management.*

During the summer of 2009, more than 60 students - undergraduates through post-doctoral students - participated in internship and student programs at the U.S. Department of Energy's Savannah River National Laboratory. The students came from all over the country, representing schools as far away as Lehigh University in Pennsylvania, Arizona State University and the University of Idaho, with many from South Carolina and Georgia. Each was paired with a mentor from SRNL's research staff and given one or more projects to work on. These projects support the Laboratory's work on behalf of DOE and the nation, while preparing the students to eventually take their place as the future of science and technology. Many of the students and mentors also value the internships as a pipeline for potential future employment at SRNL.



SRNL intern Stephen Taylor studies microbes' ability to produce energy.

The SRNL interns were among the 155 students, selected from approximately 2,000 applicants, that the Savannah River Nuclear Solutions (SRNS) Internship Office placed in internships across the Savannah River Site, including positions with SRNS, Savannah River Remediation, the Department of Energy (DOE), and several other federally funded programs. While most internships take place during the summer months, local internship participants and post-doctoral participants may remain year round.

> ***"Feeling like you make a difference always feels good."***
>
> *Andrew Romich, University of Florida undergraduate*

"We have two objectives," says Dr. Rich Dimenna of SRNL's Process Modeling and Computational Chemistry Department, who was mentor to one of the interns. "The principal one is to challenge and help develop a student. The second objective – which is lesser, especially with beginning students – is to get some useful work out of them. We're accomplishing both."

It's that "useful work" aspect that appealed to a lot of the participating students. "What I like is that we're not reproducing experiments that every student has done before you," says Whitney Jones, an Augusta State University graduate who has

held internships with SRNL's biotechnology group for two years. "It's more fulfilling than that."

Computer Simulations for Port Security

Andrew Romich, an industrial engineering undergraduate from University of Florida, came to SRNL through the U.S. Department of Homeland Security's Scholars and Fellows program, a highly competitive program that funds hand-picked students to work on homeland security-related projects at the national laboratories. "I like that I get to do research. I get to work with simulations and a lot of statistics. It seemed like something really useful," he says about his project on maritime port security. "Feeling like you make a difference always feels good."

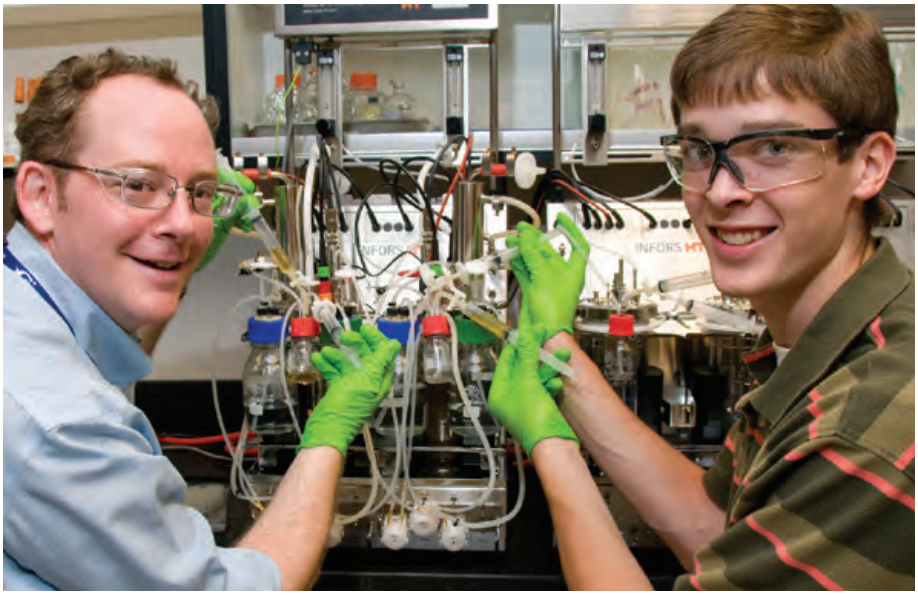
Romich's project involved computer simulations of the deployment of security resources at the nation's ports, analyzing them for ways to best use their resources to reduce radiological or nuclear security risks. Dr. Dave Dunn and Dr. Steve Harris, his SRNL mentors, appreciated both the skill and the enthusiasm he brought to the task. "He had his choice of national laboratories," Dr. Dunn says. "We're happy he chose here." Because his task was unclassified, part of his final product was a paper that SRNL is submitting for publication in one of the respected technical journals, which is a real feather in the cap of a young researcher.

Better Living Through Biology

The students also appreciate the immersion in research at SRNL. "We're more than getting our feet wet," says Jordan Burbage, a Clemson University undergraduate in biological sciences. "We're diving in to see what it's about."

"What attracted me was working with DOE and being part of the future of energy research," says Stephen Taylor, a Clemson biosystems engineering undergraduate. "Even after we're gone, the SRNL researchers can use the data we generated and get results."

Taylor, Burbage, Jones and Audrey Thompson, a Clemson microbiology undergraduate, worked with SRNL's biotechnology group on separate but interrelated projects related to the development of non-food crops like switchgrass to produce ethanol. Jack Goodell, an engineering undergraduate from the University of Michigan working with SRNL's alternative energy group, pursued a related project. Goodell pretreated the switchgrass to extract lignin, the subject of his task. What was left went to Thompson and Burbage, who were each studying how to break down one of the sugars to make ethanol. "I try to see how much yeast we want, how much sugar, what



Interns Whitney Jones (top left) and Audrey Thompson work in SRNL's environmental biotechnology laboratory.

Intern Jordan Burbage (bottom right) works with Charlie Milliken of SRNL Environmental Biotechnology.

temperature to make it the happiest and to make the most ethanol," Burbage says.

"I read a paper that says xylose [one of the sugars] can be easily degraded, but it's not easy to replicate that data," Thompson says. "You learn that in real research, things don't always work, and you go back to the drawing board, read more papers, and find another way to go at it."

Taylor's project involved the waste that will come from the ethanol production process, using its bacteria in fuel cells that will produce electricity to treat the waste, studying how to get the microbes to pump out more energy to the electrode.

Dr. Chuck Turick, who was mentor to Burbage, Taylor and Thompson, says that the group produced results needed for the program, but that the implications of their work at SRNL were bigger than that. "We get data from them. We get work done," he says. "But what's more important is to allow the students to focus on something they're interested in. Do that, and give them the equipment to use, and the data takes care of itself."

Goodell's mentor Dr. Steve Sherman found the benefits of working with interns to be both short- and long-term. "Our students today will be tomorrow's collaborators, and hopefully, person by person, we will help strengthen the Laboratory as an institution by bringing in a diverse student work force who will one day be the people we collaborate with, rely upon, or hire to help us with our work."

"We're more than getting our feet wet. We're diving in to see what it's about."

Jordan Burbage, Clemson University undergraduate

Using Math to Model Nuclear Processes

Dr. Dimenna says that SRNL got "a very nice product" from his intern Geoff Taylor. Dr. Dimenna was looking for someone with math expertise and enough background in physics and chemistry to develop a model of a portion of a nuclear process. Taylor, who graduated from Wofford in mathematics and began graduate school at the University of South Carolina (USC) in public health and epidemiology in the fall, already had experience in the computation program that SRNL planned to use for the project, and was looking for an internship related to nuclear processes, so it was a good fit for both of them. "The problem we gave him is so developmental, there is no solution yet. This is current research," Dr. Dimenna says. "He's doing preliminary work we needed that will allow us to move forward with collaborations."

"The work itself is interesting," Taylor says. "Not only that, but I work with a group of three or four professionals, and I wouldn't say I'm equal to them, but my input is considered."

Jack Goodell (above) studies lignin from switchgrass with SRNL's alternative energy research team.

Lab Experience Leads to Bragging Rights

SRNL's Michael Williams selected Caroline Johnson, an undergraduate chemical engineering student at USC, from about 80 intern resumes he reviewed, because he needed someone with her skills. In return, he worked to make sure her summer here was a valuable experience for her. "I've mentored about 30 interns in my time here. Normally, I don't even look at someone unless they are at least a junior or senior, but she had excellent laboratory experience and a lot of tools I can build on," he says. "In her application, she said she was interested in hands-on experience, and that's what we are giving her. Learning in books is two-dimensional. Here it's applied."

She appreciated the range of experiences the internship provided, which included sample collection and analysis, the testing of a new state-of-the-art technology for treating radioactive waste, and development of simulants to be used in closing the site's high-level radioactive waste tanks. "It's given me experience right off the bat. That will make it easier in my courses because, with this hands-on experience, I understand what I'm doing and why. It also lets me know that I have chosen the right field," she says. The laboratory also plans

to publish a paper about one of the projects she worked on, so she'll get credit for her contributions to the publication. "My sister, who is in grad school, has been published," she says, "but it took her a lot longer, so I get to brag about that for a while."

Working With the Researchers Who Developed the Technology

Miles Atkinson from Colorado, who graduated from Brigham Young University and began graduate work in hydrogeology at Clemson in the fall, looked at a lot of other opportunities. "Then I found out what I would be doing here, and it sounded really interesting," Atkinson says. He worked with Maggie Millings of SRNL's environmental restoration group monitoring the performance of the Savannah River Site's low level waste facilities. "We're trying to get an idea about the migration of tritium," he says. "I'm learning a lot of things I hadn't known before about groundwater and the vadose zone [the area of unsaturated soils below the surface but above the water table]. This has reinforced that I do like this field."

Brady Rambo, another hydrogeology graduate student from Clemson, worked with Brian Riha of SRNL's environmental restoration group. Both Riha and Millings appreciated the abilities that Atkinson and Rambo brought to their internships.

"Brady's background, field experience and organization have been a huge help in keeping us on track with our ARRA work" (work funded under the American Recovery and Reinvestment Act), she says. "With Miles, his geology background and experience in GIS have been a great help. He's doing data analysis, summary and final reports that will be a great help to our site customer."

Both students valued the opportunity to work at a national laboratory. "The biggest thing I've seen is that they do real science here. It's not just about getting the job done. They want to increase their knowledge. I'm impressed by that," Atkinson says.

> *"The biggest thing I've seen is that they do real science here."*
>
> *Miles Atkinson, Brigham Young University graduate, Clemson University grad student*

"A lot of the technologies they develop here are later on implemented in the environmental field," Rambo says. "So to future employers, it looks good that you've worked at a place with real research and development – cutting edge stuff." One of Rambo's projects was a "zone of influence" test for one of the SRNL-developed technologies for removing solvent contamination from the soil, to determine how far away it's having an effect, as well as analyzing grain size of sediments to determine how fast water moves through the soil layers.

Broad Spectrum of Work and Publications

This was the third SRNL internship for Beth LaBone, a USC biology/ computer science undergraduate. She has valued her summers here so much that, when her mentor asked her to recommend a student for another intern post in the same department, she suggested her long-time friend Yanina Breakiron, a chemical engineering undergraduate at Clemson, concentrating on biomolecular engineering. Both worked with Eduardo Farfan in SRNL's environmental analysis group. "This is a good introduction to a broad spectrum of work," Breakiron says. "It's given me a realistic viewpoint of what it takes to get things done. In school you do an experiment, and you're done. It doesn't work that way."

For Dr. Farfan, the best part of having the students in the laboratory was "seeing things done quickly – they're very productive." Among the variety of projects they worked on were various publications and presentations, which Dr. Farfan notes will be significant when they apply for grad school. A draft article that LaBone had worked on during her previous summers at SRNL was recently accepted for publication. Together, the students edited chapters of a Centers for Disease Control and Prevention guide for publication in a journal, providing information for medical personnel on procedures for handling radioactively contaminated patients and for preparing treatment areas for contaminated patients. Among other projects, the two also wrote or contributed to articles or presentations on SRNL's work with the International Radioecology Laboratory at the Chernobyl Exclusion Zone, and other radioecology studies.

Building a Workforce in Nuclear Safeguards

SRNL's Nuclear Nonproliferation Program sponsored a group of interns at the Savannah River Site working under the Next Generation Safeguards Initiative (NGSI), a National Nuclear Security Administration initiative to build up a future workforce for supporting international safeguarding of nuclear facilities. Some of the students worked in SRNL, and some in other parts of the site, such as the Mixed Oxide Fuel Facility (MOX), currently under construction. SRNL's program sponsor, Jeff Jay, says "NNSA recognizes the strategic significance of the upcoming retirements of the baby boomers who represent this set of core competencies in safeguards and has committed funding to support the growth of this pipeline for future safeguards professionals." Leveraging site capabilities like MOX, SRNL

and H Canyon in the assignment of the interns ensures they receive broad-based safeguards experiences with international applications. In addition to the undergraduate and graduate internships, the NNSA program expanded to include a PhD Fellowship Program in Safeguards, with two participants beginning work with SRNL in the fall.

Brady Speight, a rising senior in chemical engineering from USC, was introduced briefly to the program the previous summer and returned in 2009 working in the site's Nuclear Materials Disposition Material Control & Accountability section. "I've been busy, so I've really enjoyed it. The group I'm with is great. Along with their people skills, they have a great work ethic," says Speight. His mentor, Belvia Payne, says "Brady was an instrumental part of the Safeguards and Security team that put together a process monitoring strategy for the HB-Line facility that could ultimately lead to approximately $2.8 million in cost savings."

Zachary Maier (top) and Trevor Turner (bottom) study grout formulations for filling shutdown reactors.

Michael Dulude, who has a degree in mechanical engineering and started graduate school in nuclear engineering at the USC in the fall, worked for SRNL on remote detection systems. One of his activities involved combining two different tamper indicating seal technologies for testing and evaluation. "We expect to see some results by the end of the summer," he says. His mentor was Lee Refalo, who has worked on loan from SRNL to the IAEA staff, which provided a perspective that Dulude appreciated. "Lee has been out in the field, and seen some of this stuff being used, so he knows a lot about it," he says.

Adam Redwine, one of two Texas A&M graduate students in the NGSI program, and the first NGSI intern at the MOX facility, enjoyed the way his internship balances his academic experience. "I'm seeing a different side of the business from what I get in the classroom ," he says. "In the classroom, it's theoretical. I like that I'm getting to see the other side – how does it work in relation to society." His mentor and manager of Shaw-AREVA's Safeguards & Security Program, Dave Adkins, says, "I feel very strongly that this program has been a huge success and has had a positive impact on the project and Mr. Redwine. If all of the students from Texas A&M have the same attributes and mental attitude as Mr. Redwine, the Nuclear Renaissance will be very fortunate."

Daniel Strohmeyer, the second of two Texas A&M graduate students in NGSI, will complete his masters in health physics with a certificate in nonproliferation policy in December 2009. From the beginning of his internship, Strohmeyer was thrown immediately into review of Advanced Safeguards Approaches. "I have had a first-hand opportunity to experience the art of international collaboration, working on NNSA-IAEA safeguards projects with

three different national laboratories," he says. Mentor Dave Hanks, a six-year veteran as an international safeguards inspector with the IAEA until February 2009, was excited to have someone of Strohmeyer's caliber with a nonproliferation policy and technical background through whom he could transfer his knowledge of international safeguards to a new generation.

Hands-On Applications and Skills

Like many of the other interns, the students working with Michael Serrato and Dr. Christine Langton on the Reactor In-Situ Decommissioning project found that their internships were an eye-opening complement to a classroom education. "This lets you know what parts of your education you'll really use," says Wooten Simpson, a Clemson bioengineering undergraduate. "Like communication skills are really important. I wouldn't have known that."

Serrato says the group got experience in real engineering practice. "As a group, they participate as members of the project team. The experience is not only hands-on application and analytical analysis, but also how to communicate their results in written language, so someone can understand what they have done."

Clemson mechanical engineering/business grad student Trevor Turner, who worked alongside Simpson and Clemson mechanical engineering undergraduate Zachary Maier, explains that their interrelated projects all had to do with filling the Savannah River Site's shutdown nuclear reactors with grout. "We knew we were going into accelerated project mode, and the grout formulations were going to be key," Serrato says. "These guys are providing the manpower to develop grout formulations. Each task that these guys have been involved in and completed is a direct input into the project."

Cristian Acevedo, an undergraduate from Florida International University, worked on a related search of the scientific literature, looking at radiation effects on existing concrete. His results resolved one of the project's key questions and are being submitted for publication and presentation at a major conference.

"This lets you know what parts of your education you'll really use."

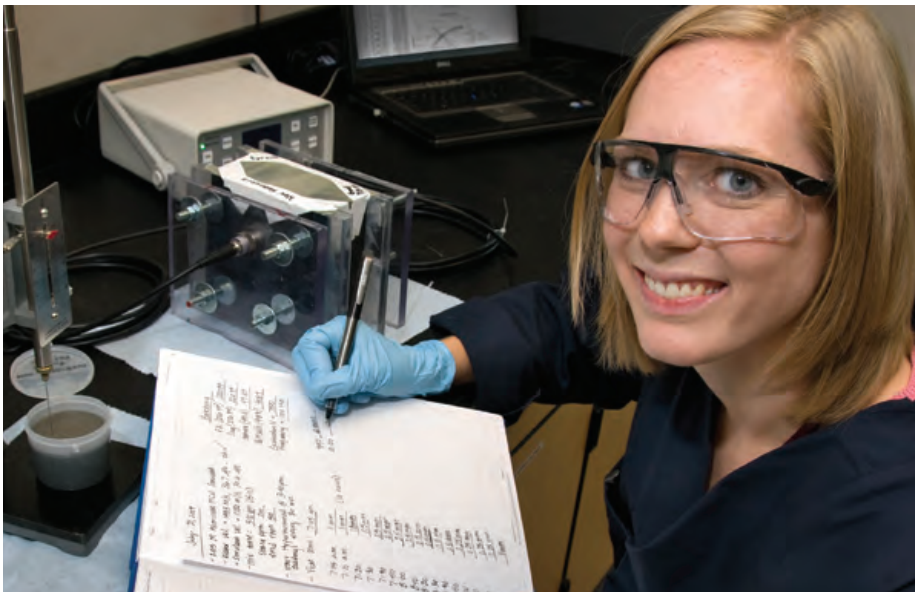
Wooten Simpson, Clemson University undergraduate

Providing a New Perspective

Katy Gustashaw, who completed her masters degree in civil engineering at the University of Texas and began work on a PhD in the fall, also worked with grout, but hers was saltstone, a specialized mixture of slag, fly ash and cement used to stabilize and dispose of a portion of the Savannah River Site's radioactive waste. Her mentor, Dr. Alex Cozzi, says that he needed someone with Gustashaw's experience for a project that uses ultrasonic sound waves to study the setting time required for the saltstone. "What we're getting with her is her background in concrete and cement research. She's providing a different perspective on how cement may interact with the other materials."

"I'm planning to do a related project for my PhD, with inorganic polymer cements," she says. "Working here is getting me acclimated to the chemistry needed for that. I think I can use some of the testing I'm doing here for the PhD work." The experience helped her confirm her plans for the future. "Having a specific project has helped me learn how to better set up a research project. It helped me to see that I really do like research. I want to be a professor, but I wasn't completely sold that I liked research, so I thought 'if I go to a research lab, maybe I'll get a different perspective,' and I did. I'm getting lots of problem-solving experience."

When Gustashaw does become a professor, Dr. Cozzi expects that her internship will have given her a familiarity with SRNL that opens doors for collaboration … and encourages her to send the Laboratory the next generation of interns.



Intern Katy Gustashaw studies setting time for grout used in waste disposal.

Awards

Dr. Carol Jantzen
of SRNL has been elected by the Board of Directors of the American Ceramic Society (ACerS) for elevation to Distinguished Life Membership in ACerS. Distinguished Life Membership is the Society's most prestigious level of membership and is awarded in recognition of a member's contribution to the ceramics profession. In over 75 years, only 130 people have been selected for this recognition.

Bond Calloway
of SRNL was selected to receive the American Institute of Chemical Engineers' Herbert Epstein Award, presented to an individual for meritorious contributions to AIChE's technical programming efforts and demonstrated dedication to the profession of chemical engineering. Bond was recognized for the revitalization of AIChE's Nuclear Engineering division and for designing and leading an institute-wide energy research survey. The survey results were published in a March 2008 Chemical Engineering Progress article "What are Chemical Engineers doing about Energy" and in AIChE's 100th Anniversary book. The award is given in memory of Dr. Herbert Epstein, a noted chemical engineer and Shell Global Solutions Operational Excellence portfolio manager.

Dr. Max Gorensek
of SRNL was elected a Fellow of the American Institute of Chemical Engineers (AIChE). This distinction is awarded by the Board of Directors of the AIChE in recognition of professional attainment and significant accomplishment in the field of chemical engineering. Dr. Gorensek is immediate past chair of AIChE's Nuclear Engineering Division.

Dr. Blythe Ashcraft Ferguson
of SRNL was given an American Chemical Society Younger Chemists Committee Leadership Award to attend the 2009 American Chemical Society Leadership Development Workshop. Twenty-six younger chemists from around the nation were invited to attend the three-day workshop in Ft. Worth, Texas. The recipients represented industry, government, and academia. In addition to attending sessions specifically tailored to younger chemists, Dr. Ferguson attended two leadership classes on effective communication and mentoring.

Dr. John Steimke
of SRNL's Engineering Development Laboratory was selected as an American Institute of Chemical Engineers (AIChE) Fellow. To attain the grade of Fellow, one has to have demonstrated significant contribution to the profession. No more than five percent of the professional members of AIChE can have the grade of Fellow. Dr. Steimke was chosen for the Shining Star Award (formerly Volunteer of Year) by the local chapter of AIChE. He has held AIChE officer positions in the local section including chair, vice chair, secretary and director.

Dr. Christopher Bannochie
was selected for the inaugural class of Fellows of the American Chemical Society (ACS). The ACS Fellows Program was created by the Board of Directors in December 2008 "to recognize members of the American Chemical Society for outstanding achievements in and contributions to Science, the Profession, and the Society." Ultimately, the body of Fellows is intended to reach approximately 1-2% of ACS membership.

Connie Herman

of SRNL has been selected as a Fellow of the American Ceramic Society (ACerS). Elevation to the grade of Fellow recognizes outstanding contributions to the ceramic arts or sciences.

Dr. Si Young Lee

was elected an American Society of Mechanical Engineers (ASME) Fellow by the ASME Fellows Review Committee. Fellow Grade, the highest elected grade of membership within ASME, recognizes exceptional engineering achievements and contributions to the engineering professions. Founded in 1880, ASME enables collaboration, knowledge sharing and skill development across all engineering disciplines, while promoting the vital role of the engineer in society.

Dr. George Wicks

has been selected to receive the Distinguished Life Member award from Alpha Sigma Mu International Honorary Society for Materials Science & Engineering. The Distinguished Life Member award, Alpha Sigma Mu's highest honor, is granted to an individual who has served the materials community and/or Alpha Sigma Mu over a long career and established an international recognition for his/her service. The award is conferred upon those select few whose technical attainment and contributions to society through leadership in the field of materials science and engineering have resulted in significant benefits to mankind.

He also has been selected to receive the American Ceramic Society/Nuclear & Environmental Technology Division's D.T. Rankin award for 2009. This award is in memory of Tom Rankin of SRNL, a long time member of the Division who served as Chair and Trustee for a number of years. The award is presented yearly to a member of the division who demonstrated exemplary service and leadership to the division.

Dr. Alfred Garrett

was awarded the 2009 Fred C. Davison Distinguished Scientist Award by the Citizens for Nuclear Technology Awareness. Over the course of his career at Savannah River, Dr. Garrett has provided sound technological solutions to a wide array of problems, ranging from reactor safety and emergency response to remote sensing and nonproliferation. He is a nationally recognized technical and scientific expert in remote sensing, with a focus on developing and applying models for data exploitation in relation to nonproliferation applications.

Dr. Joette Sonnenberg

SRNL Associate Laboratory Director for Energy Security, was named a Fellow of the American Society for Engineering Management at their annual conference in October 2009. Fellows represent less than 5 percent of the total membership and are those individuals recognized as having demonstrated distinguishing service and contributions to the society.

Dr. Don Anton

was elected Fellow of ASM International, the professional organization of the materials science and engineering profession. ASM established the Fellow of the Society honor in 1969 to provide recognition to members for distinguished contributions to materials science and engineering and to develop a broadly based forum of technical and professional leaders to serve as advisors to the society. Dr. Anton was selected for his significant and sustained contributions to materials science and technology in the areas of fatigue, superalloys, intermetallics and hydrogen storage materials and systems.

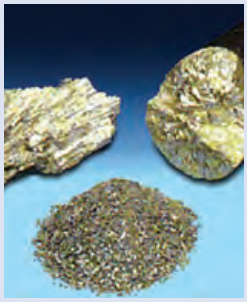
Patents

Condenser Design Enables Varying the Rate of Condensing

Patent Issued: US 7,306,029
Gary Dobos

The patent, titled "Two Part Condenser for Varying the Rate of Condensing," provides a new capability to change the rate of condensing without interrupting the system operation. This condenser design enables the unit to be used as an individual condenser or as a double coil condenser to effect different rates of condensing during experiments. The apparatus consists of a removable condenser that can be inserted into the primary, fixed condenser to increase condensing efficiency without disassembling the original set-up or interrupting the test.

Improved Hydrogen Storage Materials



Patent issued: 7,384,574
Dr. Ragaiy Zidan, SRNL, and Dr. James A. Ritter, Armin D. Ebner, Jun Wang, and Charles E. Holland, University of South Carolina

The patent titled "Hydrogen Storage Material and Process Using Graphite Additive with Metal-Doped Sodium Aluminum Hydride," provides for improved hydrogen storage materials. Adding graphite to a complex hydride such as a metal-doped alanate significantly enhances the rate at which the material absorbs and releases hydrogen, and lowers the temperature needed to release stored hydrogen.

Low-Cost Nutrient Amendments Enhance Environmental Cleanup

Patent Issued: US 7,291,265
Mark Phifer, Frank Sappington, Margaret Millings, Charles Turick and Pamela McKinsey

The patent, titled "Passive Treatment of Wastewater and Contaminated Groundwater," enhances passive bioremediation by providing low-cost nutrient amendments. The patent describes a process, requiring minimal maintenance, for long term, low-cost nutrient amendments to aquifers for bioremediation of inorganic and chlorinated contaminants.

This approach uses relatively inexpensive, biodegradable agricultural oils and waxes to provide nutrition and electrons to selected bacteria, which treat the contaminants. Since the oils float on the water to be treated and degrade slowly, they provide a steady "diet" to the bacterial community, allowing cleanup to continue without frequent attention.

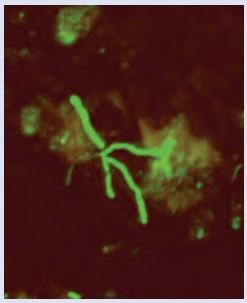
Unique, Portable Nuclear Material Detector

Patent issued: 7,351,982 B2
Charlie Fulghum, Larry Harpring, Kevin Huffman, Don Varble and Dr. Ken Hofstetter

The patent, titled "Portable Nuclear Material Detector and Process (RadRope™)," provides large scale monitoring of containers for smuggled nuclear material. The invention describes a nuclear radiation detector in the form of a rope and a process suitable for large-scale monitoring of nuclear materials in cargo-ships, buildings, warehouses, and similar structures.

This lightweight, portable system can rapidly detect the presence and location of nuclear materials in stacks of sealed containers. Using sensors arrayed linearly and encased in fabric, the RadRope system can be dangled in the 2 to 4 inch gap between stacked shipping containers on a cargo ship by a customs inspector. As the inspector walks along the top containers, a hand-held PDA shows an alarm when any sensor in the array detects radiation levels above background radiation.

Microbes for Environmental Cleanup and Oil Recovery



Two patents issued:
Environmental Bioremediation – 7,473,546
Robin L. Brigmon, Sandra Story, Denis Altman, Christopher J. Berry
Hydrocarbon Extraction - 7,472,747
Robin L. Brigmon, Christopher J. Berry

SRNL's unique, patented collection of microbes can be used both for cleaning up the environment and addressing our energy needs.

BioTiger™ resulted from over eight years of extensive work that began at a century-old Polish waste lagoon. DOE originally funded the work with the Laboratory's Polish counterparts to develop a microbe-based method for cleaning up oil-contaminated soils. From that lagoon, they identified microbes that could break down the oil to carbon dioxide and other non-hazardous products. As a result, the lagoon has been cleaned up, and deer now can be seen grazing on it.

More recent efforts have shown that BioTiger™ naturally produces chemicals that may have other industrial uses as well. For example, BioTiger™ can be applied directly for cleaning up oil residues on surfaces such as concrete slabs and building foundations.

In addition to its original environmental cleanup uses, BioTiger™ has been shown to be highly effective for increasing oil recovery from oil sands without added chemicals. Oil sands (also referred to as tar sands) represent about 40 percent of Canada's oil production, but extracting oil from these sands is more complex and requires more energy than standard oil recovery. An enhanced oil recovery process using BioTiger™ could provide a means to maximize capacity and minimize environmental impact, while remaining cost effective. The BioTiger™ microbes attach themselves to the oil sands, separating the oil from the sand particles. The microbes make the separation step easier, resulting in more removed oil and, potentially, reduced energy costs. In a test using oil sands from Ft. McMurray, Canada, BioTiger™ demonstrated a 50 percent improvement in separation over 4 hours, and a five-fold increase at 25 hours.

It may also have potential for other oil recovery initiatives, including oil shale and other underground areas with oil deposits.

Nanotech Briefs (www.techbriefs.com/nano) awarded SRNL's BioTiger™ a spot on its fourth annual Nano 50™ list, described as the top 50 technologies, innovators and products expected to revolutionize the industry.

Improved Gas Collection Apparatus

Patent Issued: 7,350,428 B2
Dennis Jackson, Kurt Peterson and Brian Riha

The patent, titled "Apparatus and Process for Collection of Gas and Vapor Samples," provides an inexpensive and reliable way to collect and transport gas samples for analysis.

The crimper apparatus allows the small, inexpensive glass vials commonly used for solid and liquid sampling to be used for gas sampling. The device was created to make gas sampling associated with environmental remediation simpler and more cost effective; existing technologies can be expensive or unreliable during air transportation.

Accurate, Easily Operated Sludge Sampler

Patent issued: 7,392,856
Thomas A. Nance, Timothy J. Steeper

The invention titled "Rotating Drum Variable Depth Sampler" is a sampling device for collecting depth-specific samples in silt, sludge and granular media. It has three chambers separated by a pair of iris valves; rotation of the middle chamber closes the valves and isolates a sample in a middle chamber for removal.

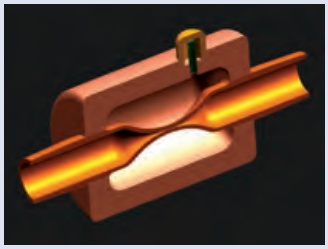
Accurate analyses of samples, regardless of the source, begins with the method for collecting the sample.

Accuracy of depth of the collected sample becomes critical, especially with rivers, lakes and ponds, storage tanks, and other soft materials that have been serially loaded with different contaminants and/or have been mixed before analytical processing. This device allows the user to capture samples at a preselected depth and to collect multiple samples in a waste burial area or a field of conventional drums.

Its design allows it to be readily manipulated by one person through a small opening such as a drum bung hole, without requiring the availability of electricity or other power sources. This is important when analyzing drums found in the woods or in a dump.

Patents *(continued)*

Expanding Hollow Metal Rings

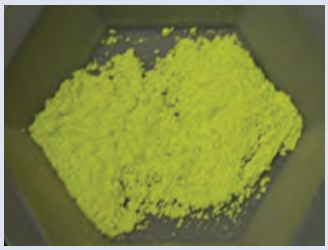


Patent issued: 7,503,594
Harold B. Peacock,
Kenneth J. Imrich

The patent titled "Expanding Hollow Metal Rings" provides a sealing device that, when desired temperatures and pressures are reached, undergoes a permanent deformation, locking the seal into place. Sealing material thickness and material composition may be used to selectively control geometric expansion, so that the seal only expands in a particular direction. The rings are useful as seals or gaskets, and may be used as passive regulator devices or shut-off devices and as inserts in pipes and tubes. They are especially useful in heated environments and especially at high temperatures.

The rings were invented for use in the extremely high temperature and corrosive environment of a facility for converting high-level radioactive waste to glass. There, they are used to lock an insert into a pour spout by expanding and deforming until it fits snugly against the extremely eroded spout.

Modified Sorbent Materials



Patent issued: 7,494,640
May D. Nyman of Sandia National Laboratories and David T. Hobbs of SRNL

Previous work had shown that monosodium titanate (MST) could be an excellent sorbent for strontium and actinides in industrial processes and waste streams. This invention treats the MST with hydrogen peroxide, significantly enhancing its sorbent capability.

Hydrogen Storage Materials in a Sol-Gel

Patent issued: 7,504,083
James W. Congdon

The invention "Process of forming a sol-gel/metal hydride composite" provides a method for creating a sol-gel matrix that contains metal granules for storing hydrogen. The result is a free-flowing granular composite material that exhibits adequate strength for handling and for compression loading within a column or reactor. The metal hydride containing composite has improved performance and handling characteristics which offer improvements in the field of hydrogen storage.

Microbial Based Chlorinated Ethene Destruction (MicroCED)

Patent issued: 7,615,153
Christopher Bagwell, David L. Freedman, Robin L. Brigmon, William B. Bratt, Elizabeth A. Wood

Scientists at SRNL have designed an efficient and reliable method to contain, reduce, and destroy chlorinated ethene (CE) plumes in the subsurface environment. Contamination due to CEs is a global problem. It is estimated that over 50,000 sites in the U. S. alone are contaminated by chlorinated ethenes.

MicroCED: Microbiological-based Chlorinated Ethene Destruction rapidly and completely converts CE to safe end products without production or accumulation of toxic by-products. MicroCED consists of a unique mixture of naturally occurring bacteria that can be introduced into a contaminated subsurface environment where they completely transform lethal CEs to safe, nontoxic end products. The versatility of MicroCED allows for it to be used as a standalone bioremediation treatment for widespread, low level chloroethene contamination or in combination with aggressive source-zone treatment technologies.

Magnetic Coupling Device

Patent issued: 7,575,389
Thomas A. Nance

This patent describes a quick connect/disconnect apparatus that is suitable for joining two items in environments where spending the time to manually insert or remove connector pins would be impractical or hazardous, such as in radioactive environments. This device uses pins that are locked into position until exposed to an appropriately positioned magnetic field. The ability to lock and unlock the connector assembly requires no additional tools or parts other than a magnetic key.

Technologies in the News

Resilient Home Program

Following a natural disaster, the faster people can safely move back into their homes, the faster the community will recover its economic footing and its vitality. "Getting people back in their homes quickly is vital for community recovery," says SRNL's Tim Smail, who leads the Resilient Home Program, which is managed by SRNL for the Southeast Region Research Initiative (SERRI, a Department of Homeland Security Program).

That's the goal of the Resilient Home Program. "We're using applied research and development to provide more effective tools, techniques, resources and information to those that experience or respond to natural disasters," Smail says.

The program treats disaster recovery as a process with four phases – assessment of the damage, response to stabilize the home as an interim shelter, rebuilding in a more durable manner, and prevention of short and long-term effects from future disasters. As a first step, they conducted an analysis to obtain a snapshot of current technology, practices, and education available to those involved in natural disasters. In addition, they surveyed builders, homeowners, engineers, government officials, insurers, and other stakeholders to determine the educational and research needs concerning natural disaster resilience.

The results showed four areas where research and education are priority needs:

- Mold assessment, response and mitigation
- Resilient rebuilding to include new materials and retrofitting
- Resilient homes to include incentive and certification programs to encourage more resilient construction
- Technology transfer of new materials available

These results were discussed and vetted by a group of approximately 65 stakeholders at the 2008 Southeastern Workshop for Disaster Resilient Homes. Based on these results, several tasks were funded. SRNL and team member North Carolina State University are responsible for projects to:

- Demonstrate "proof of concept" for self monitoring and self healing technologies that would assess, control, or repair damage
- Develop educational materials and test appropriate distribution methods to address recognized gaps in stakeholder knowledge.
- Develop and market a cost-effective national or regional (Southeastern U.S.) certification program for the higher performance of buildings.

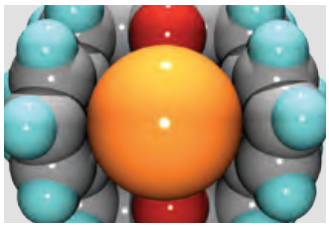
In addition, Clemson University and the Army Corps of Engineers are responsible for a project to develop resources and guidance to instruct homeowners and residents on upgrading their homes to improve resistance to natural disasters.

The goal of the Resilient Home Program is to enable community recovery following a natural disaster by dramatically speeding the return of the residents to their homes. A "test house" (bottom) for demonstrating technologies to limit damage.

About Savannah River National Laboratory

The Savannah River National Laboratory is the U.S. Department of Energy's applied research and development laboratory at DOE's Savannah River Site. The management and operating contractor for SRNL and SRS is Savannah River Nuclear Solutions, LLC. The Laboratory, established in the early 1950s to meet the Savannah River Site's technology needs, now serves DOE and the nation in three primary areas: National and Homeland Security, Energy Security, and Environmental Management. Today about half of the Laboratory's work is on behalf of the Savannah River Site, with the other half for a variety of customers in other offices of DOE, other federal agencies, and a limited number of commercial customers. One key area of responsibility is serving as the DOE Office of Environmental Management's Corporate Laboratory.

On the Cover



The cover image is an artistic depiction of a cesium atom inside the matrix of an organic extractant. This illustrates how the extractant can be used in a solvent to remove radioactive cesium from Savannah River Site salt solutions, allowing the solutions to be processed as low-level waste. Development of the solvent system occurred under the lead of Bruce Moyer at Oak Ridge National Laboratory. The molecular structure is reported in Thuéry, et al., J. Inclusion Phenom. **2000**, 36, 375.

About Science At Work

Science at Work is the flagship publication of the Savannah River National Laboratory (SRNL). It is designed to provide our Department of Energy customer, members of the scientific community, and the general public highlights of SRNL programs to put science to work in high-value R&D to serve urgent national needs.

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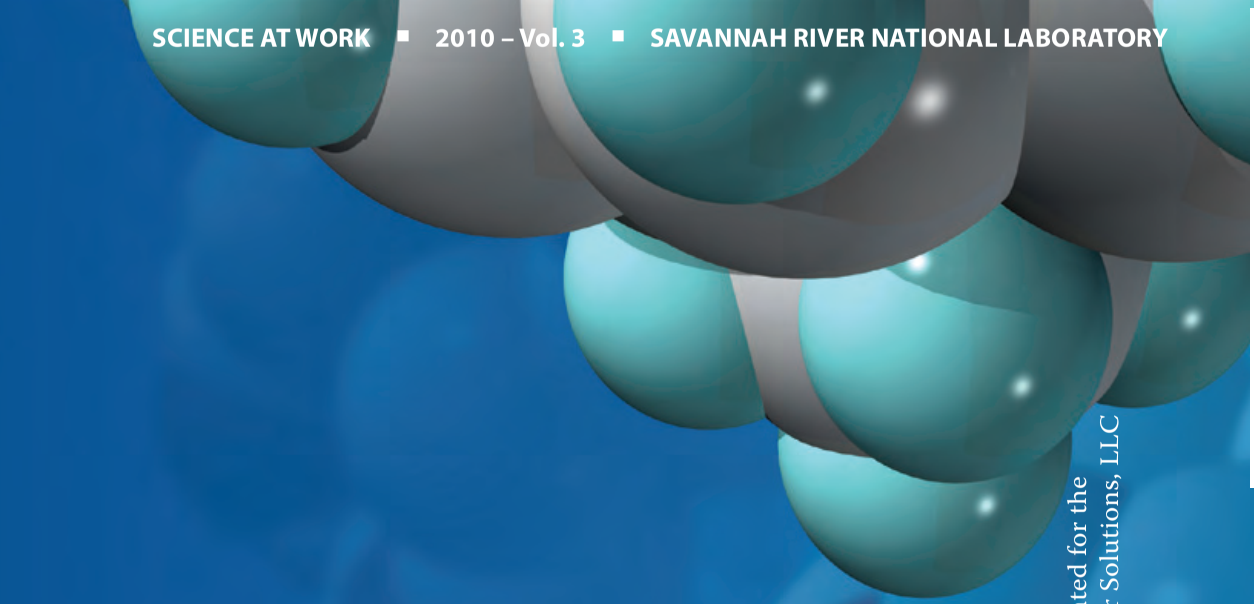

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