MPA Materials Matter

June 2013

INSIDE

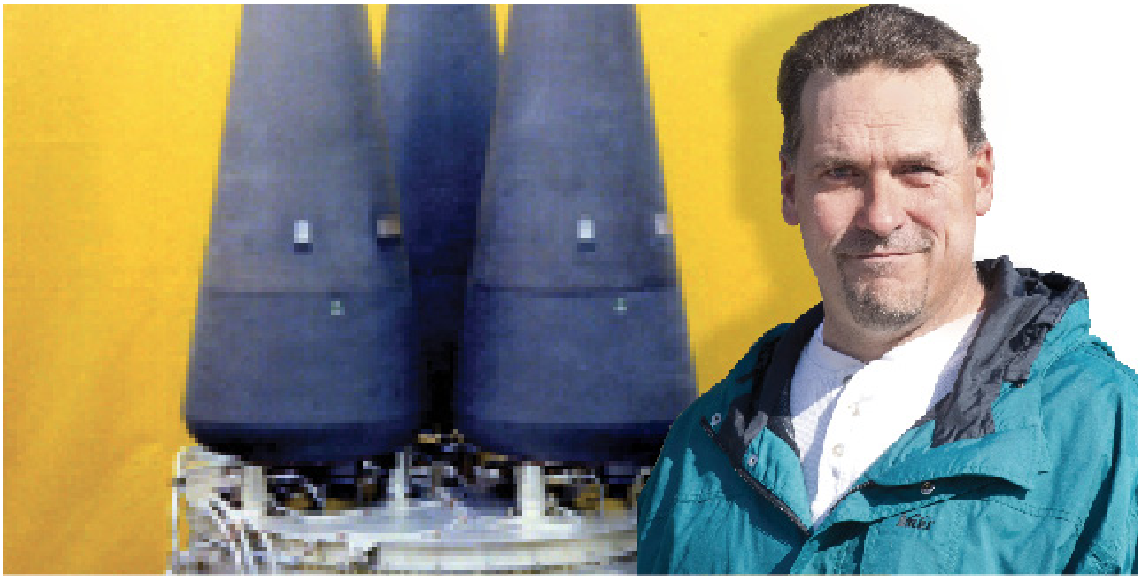


Photo by Sandra Valdez, IRM-CAS

Jon Rau

Chemist Jon Rau confronts such questions as: How can materials improve the safety and reliability of the stockpile? His team's work is synergistic with other physics and engineering efforts focused on answering these questions for aging nuclear weapons like the W78 warhead pictured above.

"LANL's primary focus on weapon materials has been from a physics and engineering perspective. Now the chemical perspective has become more predominant."

Attracted to big-picture challenges and chemistry's solutions

By Diana Del Mauro, ADEPS Communications

At the end of the Cold War, the US ban on underground nuclear tests put hefty demands on science. That's why in the late 1990s chemist Jon Rau began a new chapter in his career. He moved from basic research to investigations into how materials in nuclear weapons, which have outlived their original expiration date, are handling the aging process.

"The materials were expected to have a finite lifetime, and they have behaved quite well," Rau said. "But now they are expected to perform decades beyond what was intended."

There are many materials in a nuclear weapon, including metals, high explosives, polymers, and ceramics. The aging of any one of these materials could affect performance. If the performance of an older weapon becomes questionable, scientists must decide how to replace the aging parts in order to restore performance.

That's where Rau's work fits in. He leads a specialized team of chemists, engineers, and high-level technicians in Materials Synthesis & Integrated Devices (MPA-MSID).

"What we need to do is chemically understand these aging materials," Rau explained, "so designers and engineers have the information they need to assess when an aging

continued on page 3

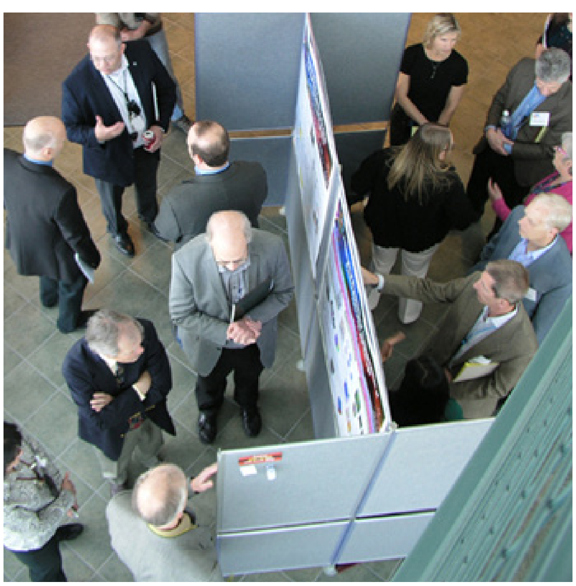
Views of the Review

The 2013 Materials Capability Review was held earlier this month and featured talks and posters by staff from across the Laboratory performing integrated nanomaterials and materials dynamics research.

The first full day of events kicked off with Principal Associate Director Alan Bishop thanking Susan Seestrom for her support of Materials for the Future at Los Alamos. Seestrom, who is the pillar's champion, is stepping down as Associate Director Experimental Physical Sciences later this year to return to research. The morning continued with MST Division Leader David Teter presenting an overview of the state of the Materials Capability at Los Alamos and MPA Division Leader Toni Taylor presenting a strategy implementation update on the Materials for the Future pillar.

MPA's David Morris, Hou-Tong Chen, Jennifer Hollingsworth, and Leonardo Civale gave talks; David Watkins led an LDRD-DR project discussion; and Min Ah Seo, Jinkyoung Yoo, Steve Gilbertson, and Scott Crooker presented posters.

Photos by Sandra Valdez, IRM-CAS, and Karen Kippen, ADEPS



From top: Alan Bishop thanks Susan Seestrom for her support of the Laboratory's Materials pillar; George Dominquez and Peggy Vigil at command central outside the review in the Study Center; Amy Clark presents research on in situ imaging of solidification during a poster session; Irene Beyerlein discusses her LDRD project with the committee; the Materials Dynamics poster session was held at CINT; the MCR Review Committee (from left, Richard Lesar, Alexandra Navrotsky, Jeffrey Lynn, Christine Orme, Gary Was, Barbara Jones (chair), Michael Kaufman, and Adam Schwartz.

Rau cont.

material will have a negative impact on weapon performance." His team's research, in many cases, reinforces confidence that certain materials are still viable. It's part of a body of research that allows the nation to extend the life of weapons rather than remanufacture weapons every few decades, which is tremendously expensive.

During the Cold War, researchers designed and built nuclear weapons using materials that could be tested in underground nuclear tests. Now aging weapons are "tested" in computer simulations, which require a more complete understanding of weapon materials because a simulation must accurately predict how weapons parts behave during the detonation. "LANL's primary focus on weapon materials has been from a physics and engineering perspective," Rau said. "Now the chemical perspective has become more predominant."

Keys to Rau's success

"I've had a pretty wild career," said Rau, flanked by a world map and a chart of nuclides in his building's conference room. "The opportunities here are what you make of them. The more creative you are, the better the opportunities."

Rau set out to be an engineer, but during college he grew interested in chemistry and participated in LANL's undergraduate student program, where he was involved in environmental sequestration research. After he received a master's degree in physical chemistry from the University of Wisconsin-Madison, the Laboratory's Chemical Sciences and Technology Division hired Rau 16 years ago as a technician to help study heterogeneous catalysts for selective oxidation of organic compounds and purification of diesel exhaust. Today, as a technical staff member in MPA he leads a number of materials-related R&D projects. He builds teams of scientists and engineers to solve a variety of problems relevant to the Weapons program, not just aging.

His team's biggest accomplishment—developing new materials in the interest of nuclear weapons safety—is about to come to fruition after five years of work. "It's very different from traditional work, and the military's in love with it," Steve Renfro, Weapons Engineering and Experiments acting deputy associate director, said. "People with 'general' and 'admiral" in their titles are talking about it."

Next, Rau will expand the Laboratory's ability to advance plutonium science. As part of a larger mission to reestablish crucial capabilities, which LANL leaders say have "suffered from post-Cold War neglect," Rau's team will develop new process chemistries to recover and recycle scarce isotopes and explore the use of plutonium-242 in research. LANL's Plutonium Science and Research Strategy explains the benefit: "Having a radioactivity some 16 times lower than plutonium-239, meaningful quantities of plutonium-242 metal and alloys can be used in radiological facilities that function under lower security and lower hazard levels ... and where the national laboratories have unique instrumentation and capabilities to conduct state-of-the-art science."

Renfro attributes Rau's success to a handful of attributes: 1) He's a big-picture thinker, taking in the expanse of the Laboratory, the nation, and world politics as he goes about his business. 2) Before concocting new mixtures of chemicals, Rau extrapolates how various combinations could solve a problem the nation has been wrestling with for decades, or throw a troublesome kink in those efforts. 3) Moreover, Rau is a master listener who lives by the axiom, "If you're not listening, you're not understanding the problem."

Jon Rau's Favorite Experiment

What: Development of a hydrogen-generating foam

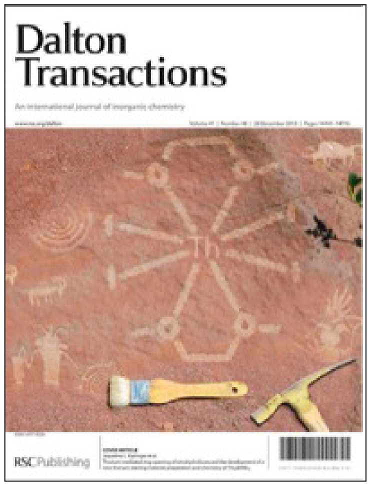
When: 2008

Where: TA-48 Los Alamos National Laboratory

How: A colleague, Troy Semelsberger (Materials Synthesis & Integrated Devices, MPA-MSID), and I were developing a material that was capable of becoming a foam that liberated copious amounts of hydrogen under certain conditions and remained completely innocuous under others. We were confident we had a mixture that was stable under some pretty severe conditions and were exploring ways to induce the foaming reaction by introducing various liquids to help facilitate the reaction.

The a-ha moment: We realized we had found a suitable combination when our reaction vessel began to expel hydrogen through the vent we were using to allow it to escape. It became apparent rather quickly that we had underestimated the rate of hydrogen generation and the size of the vent. Thankfully, we had also planned for an overpressure condition but the reaction was happening so fast my colleague had no choice but to aim the vessel in a safe direction and wait for the pressure relief to give way. For a few seconds, he looked like Wile E. Coyote in a Bugs Bunny cartoon holding a stick of dynamite in one hand and plugging his ear for the upcoming explosion with the other. When the reaction was complete we had a good laugh and a material that we were looking for.

New non-metal routes to thorium starting materials



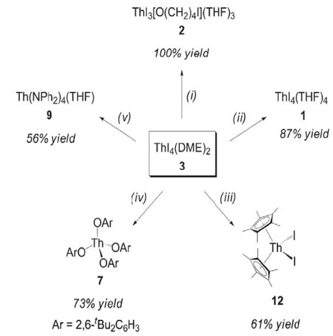
Journal cover illustrates the stable and versatile thorium iodide starting material, ThI4(DME)2, which is prepared using a non-thorium-metal route. ***Image courtesy of Anthony Mancino (IAT-1).***

One of the key breakthroughs in inorganic and organometallic thorium chemistry was the development of a convenient synthesis of the Lewis base adducts, $ThX_4(THF)_4$ (X = Br, I; THF = tetrahydrofuran), by a team of Los Alamos chemists in 1992. The researchers prepared $ThX_4(THF)_4$ complexes under mild conditions by dissolving thorium turnings with elemental bromine or iodine in THF. This solution route represents a significant advance over previous methods to thorium tetrahalides, ThX_4 (X = Cl, Br, I), which required special equipment, hazardous reagents, and high temperatures. Since then, thorium metal has become increasingly difficult to obtain. This shortage has greatly hindered the ability to perform much-needed thorium research in chemistry, materials science, and fuel cycle applications.

Jaqueline L. Kiplinger (MPA-MSID) led a team that developed a better approach to produce the thorium (IV) tetraiodide complex, ThI4(DME)2 in high yield. This route avoids the use of thorium metal as a reagent and represents a powerful new strategy for accessing thorium research. *Dalton Transactions* published the new research and featured it on the journal cover.

The new strategy reacts $ThCl_4(DME)_2$ (DME = 1,2-dimethoxyethane) with excess trimethylsilylidodide (Me_3SiI) at room temperature to produce the thorium(IV) tetraiodide complex, $ThI_4(DME)_2$ in high yield. Previously, Kiplinger's team reported the simple preparation of $ThCl_4(DME)_2$ in quantitative yields from thorium nitrate. They showed that the classic Lewis base complex $ThI_4(THF)_4$ is more unstable than previously believed and characterized the first examples of THF ring-opening mediated by thorium. In contrast, thermally stable $ThI_4(DME)_2$ can be used to prepare a variety of thorium compounds and materials on multigram scales (see figure). The synthetic accessibility and versatility of $ThI_4(DME)_2$ suggest that it will be a valuable reagent for expanding the chemistry of thorium iodides.

Synthesis of of Th(IV) alkoxide, amide, and organometallic complexes from $ThI_4(DME)_2$.



Reference: "Thorium-mediated Ring-opening of Tetrahydrofuran and the Development of a New Thorium Starting Material: Preparation and Chemistry of $ThI_4(DME)_2$," *Dalton Transactions* **41**, 14514 (2012). The journal's editor featured the article on the journal cover and highlighted it in a subsequent article on the *Dalton Transactions* blog. Materials Synthesis and Integrated Devices (MPA-MSID) coauthors include Nicholas E. Travia (Seaborg Postdoctoral Fellow), Marisa J. Monreal (Reines Postdoctoral Fellow), Brian L. Scott, and Jaqueline L. Kiplinger.

The Laboratory Directed Research and Development (LDRD) program and the DOE Office of Basic Energy Science - Heavy Element Chemistry program funded different aspects of the work. The research supports the Laboratory's Energy Security mission area and the Materials for the Future science pillar.
Technical contact: Jaqueline Kiplinger

RSI spotlights new device for measuring acoustic properties of fluids

Research describing a portable measurement cell, invented by Sensors & Electrochemical Devices (MPA-11) scientists for evaluating the acoustic properties of fluids at high temperatures, high pressures, and in chemically and mechanically harsh environments, has been selected as a 2012 Research Highlight by editors of *Review of Scientific Instruments*. This distinction is given to fewer than 10% of the journal's articles.

Similar in size to a hotdog in a bun, the measurement cell represents an advancement in the established room temperature swept frequency acoustic interferometry measurement for liquid sound speed determinations. To demonstrate the measurement cell, the researchers compared their data to the internationally accepted standard, IAPWS-IF97. The precision achieved with the measurement cell is shown to be significantly better than 0.1%. The team also reported two sets of experimentally measured sound speeds in liquid water. The first set of data showed sound speed as a function of temperature up to 250°C at pressures corresponding to the liquid-vapor coexistence line. The data in the second set were collected near room temperature as a function of pressure up to 3000 psig. Although significant work exists in the literature on the characterization of fluids, primarily pure water, over a wide range of pressures and temperatures,

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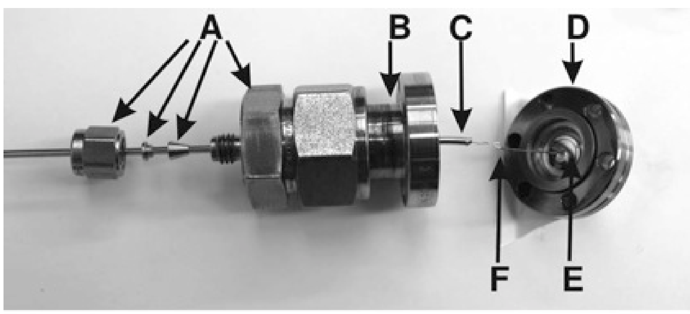
RSI cont.

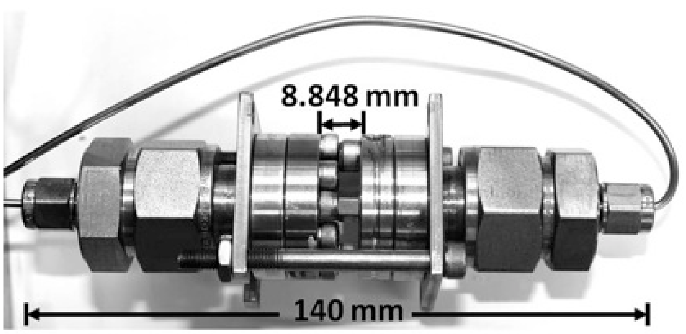
the availability of experimentally determined sound speed in water between 100° C and 250°C is limited. The need to measure sound speed in liquids up to 250°C is of both fundamental interest, as in the case of basic equations of state, and applied interest, such as for characterizing geothermal or petroleum downhole environments.

Reference: "An acoustic resonance measurement cell for liquid property determinations up to 250°C," by Blake T. Sturtevant, Cristian Pantea, and Dipen N. Sinha (MPA-11), *Rev. Sci. Instrum.* **83**, 115106 (2012). The DOE funded the work, which supports the Laboratory's Energy Security mission and its Materials for the Future and Science of Signatures pillars.

Technical contact: Blake T. Sturtevant



(a)



(b)

A stainless steel package protects the measurement cell's transducers, two lithium niobate ($LiNbO_3$) crystals, from mechanically and chemically harsh test environments.

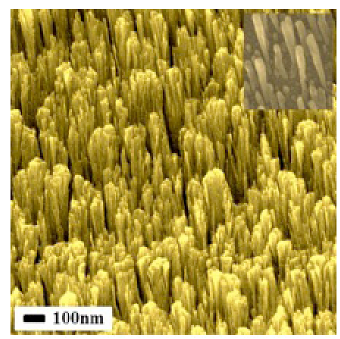
(a) The construction of a packaged high temperature and pressure acoustic transducer including a 2 mm-0.75^2 Swagelok union (A), 1-1/3^2 Conflat half-nipple (B), high temperature stainless steel sheathed coaxial cable (C), 1-1/3^2 Conflat blank flange with a custom well 3.2 mm deep x 12.5 mm in diameter bored out (D), a 5 MHz 36° Y-rotated lithium niobate transducer (E), and a flexible Kapton insulated wire (F) for making the connection between the coax center conductor and the transducer.

(b) Two packaged transducers arranged opposing each other for transmission mode SFAI measurements. The length, L = 8.848 mm, of the resonant cavity is defined by the bolt heads with spacers used to hold the CF flange together. The measurement cell is compact at 14 cm in length.

Realizing the smallest possible nanopillars using physical vapor deposition

Arrays of thin noble-metal nanopillars, also referred to as nanorods or nanowires, have enormous potential for catalysis as well as other applications where a large surface-to-volume ratio is desired. One particularly crucial unknown, however, is the minimum diameter nanorod achievable by physical vapor deposition (PVD), a versatile method for fabricating nanostructures from essentially any material. So far, diameters down to 50 nanometers (nm) have been reached with PVD, but experimentalists would benefit from having a clear minimum-diameter target in sight.

A recent article in *Physical Review Letters,* based on work at the Center for Integrated Nanotechnologies (MPA-CINT) at Los Alamos National Laboratory, presents a model and experimental results showing that this minimum size could be much smaller than previously thought.



Scanning electron micrograph of Au nanopillars (diameter approximately 7 nm) made by physical vapor deposition (PVD).

Solid films grown by PVD are usually fabricated one layer of atoms at a time, but to grow axial nanostructures, one has to build up multiple partial or incomplete layers on the substrate. Theoretical models of this process haven't taken into account multilayered surface steps in the early growth phase because they were thought to be too kinetically unstable to have an effect on the final structure. The current work shows that these surface steps are, in fact, important because they dictate how the next layer of adatoms will position themselves. The researchers found that growth conditions favoring multilayered surface steps over monolayer steps are the key to growing small, well-separated nanopillars.

Optimizing the growth conditions such as the choice of substrate, substrate temperature, and the rate and angle of deposition, it was shown that well-separated nanorods with diameters of 20 nm for copper and 10 nm for gold should be possible, a prediction that was verified with electron micrographs of actual nanopillars prepared in the lab.

Reference: "Smallest Metallic Nanorods Using Physical Vapor Deposition," by Xiaobin Niu, Stephen Stagon, Hanchen Huang (University of Connecticut) and J. Kevin Baldwin and Amit Misra (MPA-CINT), *Physical Review Letters* **110**, 136102 (2013). The work is a collaboration between Huang's materials theory group at the University of Connecticut and CINT at Los Alamos. Huang's group accessed the CINT

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Nanopillar cont.

physical synthesis lab through an approved user proposal. CINT is a national user facility sponsored by the DOE, Office of Science, Office of Basic Energy Sciences. This work on the science of nanopillar materials is aligned with the Laboratory's Energy Security mission and Materials for the Future pillar.

Technical contacts: J. Kevin Baldwin and Amit Misra

MPA research featured in APS March Meeting 2013 invited talks

Five Materials Physics & Applications (MPA) scientists presented invited talks at the world's largest physics gathering, the annual American Physical Society's March Meeting, held in Baltimore, Maryland.

In "Time-resolved ARPES and f-electron coherence," Tomasz Durakiewicz (Condensed Matter & Magnet Science, MPA-CMMS) presented examples of time-resolved ARPES (angle-resolved photoemission spectroscopy) measurements of f-electron systems, providing valuable information about the evolution of coherence and the dynamics of the related quasiparticle states. The Laboratory Directed Research and Development (LDRD) program and the DOE Office of Basic Energy Sciences (BES) Division of Materials Sciences and Engineering supported the work.

While the vast majority of materials can be investigated using photoemission at public synchrotrons, transuranic materials are excluded from these facilities. In "Transuranic photoemission using a unique light source," John Joyce (MPA-CMMS) described the Laboratory's advanced spectroscopy capability for photoemission on transuranic materials, including plutonium. The Laser Plasma Light Source is a unique spectroscopy facility at Los Alamos run by Joyce, Tomasz Durakiewicz, and Kevin Graham. He also presented examples, using several different photoemission variants, which explored a range of plutonium materials and have led to a significant improvement in understanding transuranic electronic structure. The research is supported by DOE/BES Materials Sciences and Engineering Division, LANL Science Campaign 2, and the LDRD program.

The thermal expansion of some actinides metals is strongly dependent upon doping. In "Anomalous thermodynamic behavior in actinides,"Arkady Shehter (MPA-CMMS) presented research, performed at the National High Magnetic Field Laboratory-Pulsed Field Facility, suggesting that the anomalous thermodynamic behavior in these systems has dynamic rather than static origin. The National Science Foundation, the LANL LDRD program, and the Seaborg Institute funded the work.

In "Observation of ^{239}Pu NMR in PuO_2: A new frontier for the physics and chemistry of plutonium compounds," Hiroshi Yasuoka (MPA-CMMS, Japan Atomic Energy Agency) reported on the first observation of plutonium-239's nuclear magnetic resonance signal, for which researchers have searched for more than 50 years. The findings potentially open a new horizon for the solid-state physics, nuclear materials science, and complex chemistry in plutonium compounds. Collaborators include Georgios Koutroulakis, Eric Bauer, and Joe D. Thompson (MPA-CMMS), David L. Clark (National Security Education Center, NSEC), Gordon Jarvinen (Seaborg Institute), Scott Richmond and Alice Smith (Nuclear Materials Science, MST-16), and Douglas Veirs (Actinide Processing Support, MET-1). This work was supported by the DOE/BES Chemical Sciences, Geosciences, and Biosciences Division and by the Materials Sciences and Engineering Division, the LDRD program, and the LANL Seaborg Institute.

In "High-performance electrocatalysts for oxygen reduction derived from polyaniline, iron, and cobalt," Piotr Zelenay (MPA-11) described the development of a family of non-precious metal oxygen reduction reaction catalysts capable of minimizing the performance gap to platinum-based catalysts at a cost sustainable for high-power fuel cell applications. The approach utilizes polyaniline as a precursor of a carbon-nitrogen template for high-temperature synthesis of catalysts in the presence of transition metals (Fe and/or Co). Invited speaker Raymond Orbach, director of the Energy Institute at the University of Texas at Austin and former undersecretary for science in DOE, referenced this talk in his presentation about fossil fuel use and carbon dioxide emissions. LDRD and DOE's Hydrogen and Fuel Cells Program supported the work.

For more information, please see meetings.aps.org/Meeting/MAR13/APS_Invited.

Celebrating service

Congratulations to the following MPA Division employees celebrating a service anniversary recently:

James Boncella, MPA-MSID ....10 years
Hoon Chung, MPA-11 ....5 years
Kimberly Modic, MPA-CMMS ....5 years

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To submit news items or for more information, contact Karen Kippen, ADEPS Communications, at 505-606-1822, or kkippen@lanl.gov.

To read past issues, see www.lanl.gov/orgs/mpa/materialsmatter.shtml

Los Alamos NATIONAL LABORATORY EST. 1943

Remaining safety aware

Two recent events within the Directorate underscore the importance of remaining vigilant in making safety integral to Laboratory operations. For each, HPI (Human Performance Initiative) Learning Teams were assembled. Thanks go to these members who spent much time and effort to produce valuable feedback, which is summarized and shared here.

In the first instance, an MPA-11 graduate student worker received minor splashing to the forehead and wrist from a 10% concentration of sodium hydroxide (NaOH) after failing to open an exit valve on an experiment. The resulting pressure build up caused a rubber stopper to pop off and discharge the chemical. After flushing face and eyes at an eyewash, the worker was transported to Occupational Medicine, ultimately being referred to an eye specialist for further evaluation of the minor injury.

The biggest contributing factor to this event was scope being added to an experiment (adding a NaOH bubbler/scrubber) and insufficient attention being paid to the new hazard and associated controls. This was an unusual experiment for this team in that a hazardous chemical (NaOH) was being used in the measurement lab, instead of the chemistry lab.

Main lessons learned from this event:

- Be aware of scope creep. Implement an experimental review process using a graded approach when experimental changes are made in R&D work, including consideration of the degree of thought required in planning the next experiment.
- Wear safety glasses or goggles as required; order prescription safety glasses if necessary.
- Explore/encourage the use of experimental plans/planning meetings to bridge the gap between IWDs (integrated work documents) and actual R&D work.

In the second instance, a hose on a subsystem of Physics Division's vertical shock tube burst while it was being tested after changes to a subsystem. Workers were wearing hearing protection per the recommendation in the IWD, however, adjacent workers were not, and the resulting noise was significant enough to cause two workers to go to occupational medicine; no one withstood permanent hearing loss.

A review of the event revealed that while the Pressure Safety Officer had inspected and approved the air subsystem change, a further modification was made–the addition of a nozzle to the system–afterwards, without a further PSO inspection. It was this nozzle that allowed pressure to build and overpressurize the hose past its rating.

Main lessons learned from this event:

- If you share space with multiple operations owned by different groups–as was the case here–ask the owner of the space to provide updates about activities, hazards, and details on what constitutes normal vs. off-normal events.
- Understand the formality of operations and follow change control processes.
- Know who your safety officers (pressure, electrical, and laser) are and what changes in work warrant an inspection.
- Ensure all components in a pressure system are rated to the highest achievable pressure in the system.
- Understand what constitutes an off-normal event and how to react to one, e.g., stop work and notify the PIC (person-in-charge) and/or group office.

HeadsUP!

Good housekeeping equals good safety

In this season of spring cleaning, the Target Fabrication Facility (TFF) has a success story to share.

Last year, TFF residents, which includes members of Polymers & Coatings (MST-7), began a massive cleanup effort in their 85,000-square-foot facility. In addition to recycling 15 tons of metal and 2 tons of wood, the group eliminated 170 boxes of documents, downsized from 45 to 9 safes, and sent 250 notebooks to Records Management. A new chemical stock room, where 3,000 chemicals were consolidated, reduces the number of chemicals needed to be ordered and promotes sharing common resources with other facilities.

In the process the residents changed the culture so excess materials won't pile up again. The group has restored a sense of pride in time for the TFF's 30th anniversary and set an example of how to Clean the Past, Control the Present, and Create a Sustainable Future, three long-term Laboratory Environmental Management System Environmental Stewardship & Sustainable Strategy goals in the FY13 Site Sustainability Plan.

In recognition of their efforts, the "TFF 30th Anniversary Housekeeping Initiative" received a Silver Award in the Change Agents category for the Laboratory's 2013 Pollution Prevention Awards.

Commonly used chemical supplies are now consolidated in a well-organized stock room.

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