Transforming Explosive Art into Science

For centuries, intuition and trial and error dominated the development of high explosives. Now, high-explosives researchers at Lawrence Livermore are imposing more rigorous scientific structure and techniques upon their work.

FEW products typically take years of effort to synthesize yet disintegrate in a few millionths of a second when used. Despite their brief lifespan, energetic materials, particularly high explosives, are in demand as never before by the Department of Energy, Department of Defense, and industry for their unique properties: shock waves producing pressure up to 500,000 times that of Earth's atmosphere, detonation waves traveling at 10 kilometers per second, temperatures soaring to 5,500 kelvin, and power approaching 20 billion watts per square centimeter.

Explosives have been around since Chinese gunpowders appeared during the 11th century. However, until the past 15 years, their development has been characterized by an approach based largely on intuition and trial and error. Now high-explosives scientists are imposing more rigorous scientific structure and techniques upon all aspects of their work.

For example, Lawrence Livermore researchers are combining breakthrough computer simulation codes, state-of-the-art experimental diagnostics, and a culture in which theoretical, synthesis, and experimental chemists and physicists work alongside each other. At the same time, they are working more closely with their partners in the energetic materials community, from DOE's Pantex Plant in Texas to the Air Force's Wright Laboratory at Eglin Air Force Base, Florida, to small explosives companies in the San Francisco Bay Area.

Advances in energetic materials, which include high explosives, propellants, and pyrotechnics, benefit DOE's Office of Defense Programs, DoD's warheads and propulsion efforts (especially the 12-year-old DOE/DoD "Memorandum of Understanding on Conventional Munitions"), NASA's space exploration programs, the Federal Aviation Agency's explosive detection efforts, and many industries, including mining, oil exploration, and automobile. The continuing demand is driving a search for better theoretical models of the behavior of energetic materials and an improved diagnostic capability to measure the complex chemical and hydrodynamic processes during detonation.

According to Ron Atkins, director of the Energetic Materials Center (EMC), a joint effort of Lawrence Livermore and Sandia National Laboratories, U.S. industry has scaled back its energetic materials research because of safety and financial considerations. Likewise, the Department of Defense's own energetic materials research faces significant budget pressures, while academia does not have the costly facilities to carry out such research. As a result, says Atkins, "the national labs are becoming the country's most important repository of energetic materials expertise." Atkins is heading a task force representing several Livermore directorates in work to ensure that the Laboratory will remain a national resource for energetic materials expertise over the next decade and beyond.

Livermore researchers have studied and synthesized high explosives for decades because they are an integral element of every nuclear weapon. Today, under the EMC umbrella, their work encompasses a wide range of basic research and programmatic activities. Lawrence Livermore chemists are synthesizing new compounds that yield more energy, are safer to store and handle, and are less expensive and more environmentally friendly to produce. They also are designing new paths to synthesizing existing energetic molecules that are cheaper and easier on the environment.

Understanding Is Key Goal

Livermore scientists are conducting experiments to better understand the fundamental physics and chemistry of energetic materials, particularly with regard to their stability, sensitivity, and performance. "Despite a century of work, scientists still do not understand what happens in a detonation wave thoroughly enough to predict all the details of how a given explosive will behave under various conditions," says Randy Simpson, head of the Energetic Materials Section in the Chemistry and Materials Science Directorate.

Simpson and his colleagues are also involved in fundamental surveillance activities associated with the maintenance of the nation's nuclear weapons stockpile. Performance and safety testing (see *Science & Technology Review*, December 1996, pp. 12–17) assures that the high explosives in nuclear warheads will remain dependable despite decades of storage. Another aspect of stockpile stewardship work is developing safe and environmentally sound methods for dismantling and disposing of thousands of kilograms of high explosives removed from retired nuclear weapons. Going a step further, Livermore chemists are investigating processes that would permit the reuse of these high-quality, expensive materials in the commercial marketplace.

Table 1. Codes used in developing energetic materials.

Code	Function
ALE3D	Hydrodynamic code used in safety analyses such as "cookoff" simulations spanning a remarkably wide time span. (Developed at LLNL.)
CHEETAH	Transforms predicted formation energy and density of molecules into performance measures such as detonation velocity, pressure, energy, impulse, and impetus. (Developed at LLNL.)
GAUSSIAN	Determines the three-dimensional shape of the molecule and the energy binding its atoms.
MOLPAK	Packs molecules together into a low-energy configuration.
TOPAZCHEM, PALM	Predict changes in thermal and chemical properties caused by different accident, battlefield, and aging scenarios. (Developed at LLNL.)

Figure 1. (above) Livermore's High Explosives Applications Facility (HEAF), completed in 1989, is playing a major role in developing and characterizing high explosives. (right) Specially designed containment vessels are used to safely detonate high explosives in quantities as large as 10 kilograms of TNT-equivalent.

Guiding all of these activities are computer codes that mimic energetic materials and the very rapid physical and chemical processes that govern their detonation (Table 1). The codes reflect longstanding Livermore expertise in simulating extremely short-lived events such as nuclear detonations. Continually refined by experimental data, the codes are paving the way for an unprecedented understanding of energetic materials at the molecular level.

The work is headquartered in the High Explosives Applications Facility (HEAF) at Livermore, which represents the state of the art in high-explosives research with regard to both technical capability and safety (Figure 1). Work at HEAF is complemented by activities some 15 miles away at Site 300, where large-scale high-explosives processing and testing are carried out.

Searching for New Materials

Simpson notes that in a world accustomed to daily announcements of important scientific advances, breakthrough high-energetic materials have been few despite steady progress in explosive power and insensitivity over the past century. The last energetic material to "hit it big" was HMX (cyclo-tetramethylene-tetranitramine), discovered during World War II as a contaminant in a batch of another explosive material. Since then, Simpson says, there have been TATB (triamino-trinitrobenzene, a highly insensitive high explosive for nuclear weapons) during the 1970s and a few specialty materials, but certainly nothing used as widely as TNT (trinitrotoluene) (Table 2).

The reason for the paucity of new energetic materials is the fact that they must meet so many different requirements such as high energy density, insensitivity to mechanical insults, resistance to chemical decomposition, inexpensive synthesis from readily available reagents, and the ability to be formulated with other materials for fabrication into practical devices.

Despite the difficult requirements, Livermore chemists are optimistic that they can improve the safety and performance of current and future weapons systems. It is a balancing act because the compounds must be powerful enough to do the job and at the same time insensitive enough to prevent accidental explosion. For some applications, the priority is on improving safety, especially with nuclear weapons and with explosives stored on ships.

For other applications, higher power and energy are of greatest interest. (Energy is the capacity of an explosive to do work, whereas power is the rate of energy release, or how rapidly the explosive can accelerate metal. Energy is measured in joules, power in joules per second.) In this area, several new Livermore explosives have been developed for Air Force weapons directed at penetrating "hard targets" such as underground reinforced concrete bunkers. In the same performance arena, smaller shaped charges using Livermore formulations are demonstrating velocities up to 10 kilometers per second to penetrate thick steel armor plate some 6 to 8 times the diameter of the shaped charge.

Developing new energetic materials is a complicated process in which many candidate molecules are considered, a few synthesized, even fewer formulated, and only a small handful adopted by the military or industry. The laborious process involves computer modeling, plenty of laboratory work, and thorough testing.

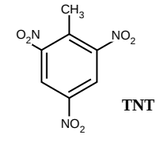
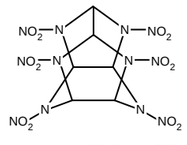
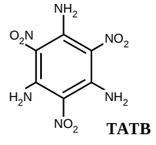
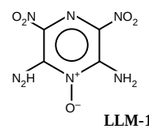
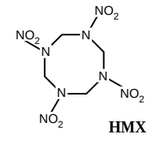
Starting at the Chalkboard

The road to a new high explosive begins the old-fashioned way, when candidate molecules are drawn on a chalkboard by both theoretical and synthesis chemists. Theoretical chemists tend to suggest more "flamboyant" molecules than the synthesis chemists because they have less experience in the laboratory, quips theoretical chemist Larry Fried. Once a group of candidates is agreed upon, Fried and his colleagues take over, screening the molecules with a host of computer codes.

The codes help guide the synthesis chemists by predicting the inherent characteristics of the cyber-compounds. Fried says the process is similar to that found in the pharmaceutical industry. In that business, too, trial and error and human hunches used to be predominant, but now sophisticated computers are helping to point the way to prime-candidate molecules for synthesis.

Livermore high-end workstations do simulations with the speed that approaches a supercomputer's. The software program GAUSSIAN (used widely in the chemical and pharmaceutical industries) is first

Table 2. Molecular structure of important energetic materials.

Material	Molecular Structures
TNT (trinitrotoluene)	 TNT
HMX (cyclo-tetramethylene-tetranitramine),	 CL-20 in LX-19
TATB (triamino-trinitrobenzene)	 TATB
LX-19 (2,4,6,8,10,12-hexanitro-2,4,6,8,10,12-hexaazaisowurtzitane, which is CL-20, plus a polymer binder)	
LLM-105 (2,6-diamino-3,5-dinitropyrazine-1-oxide)	 LLM-105
	 HMX

employed to determine the three-dimensional shape of the molecule and the energy binding its atoms. The molecules are then "packed together" into a low-energy configuration for greatest stability by another widely used program called MOLPAK.

Finally, CHEETAH transforms the molecules' predicted thermodynamic energy and density into explosive performance measures such as detonation velocity, pressure, and energy (Figure 2). CHEETAH, developed by Fried and his colleagues, is a thermochemistry code derived from more than 40 years of experiments on high explosives at Livermore. With libraries of hundreds of reactants and 6,000 products in its code, the program is now used throughout the world and has become DOD's preferred code for designing new explosives and, to a lesser extent, propellants and pyrotechnics (see *Science & Technology Review*, June 1996, pp. 6–13). The capabilities of the massively parallel computers in DOE's Accelerated Strategic Computing Initiative (ASCI) at the Laboratory are being used to assist with modeling the hydrodynamics of candidate explosives, and plans call for ASCI's use in creating advanced predictive models of the chemical reactions that occur when candidate molecules explode.

Assuming the software programs validate the chemists' premise that the candidate molecule offers significant potential, the material is ready to be synthesized.

Synthesis Can Be Tough

While it takes about one week to screen a candidate molecule by computer, its actual synthesis in the laboratory can require a year or even longer of painstaking effort.

"It takes a lot of trial and error to get the synthesis reactions to go," says organic chemist Phil Pagoria (Figure 3). "The chemist must constantly evaluate whether the project is progressing or whether the molecule, as planned, is impossible. It is an iterative process, depending largely on the knowledge, abilities, and intuition of the chemist. Many times, a synthesis scheme cannot be considered for full-scale production because it ultimately requires too many steps or reagents that are too costly."

Much of the synthesis effort is devoted to developing new energetic materials that possess an energy density (the energy that can be released from a specified volume of material) at least 15% greater than that of HMX, the high-energy high explosive against which candidate materials have long been evaluated. HMX replacements are needed for a host of volume-fixed armaments such as so-called smart, or precision-guided, munitions.

Many have been developed at Livermore. One formulation, LX-19, is the highest power material in the world but somewhat more sensitive than

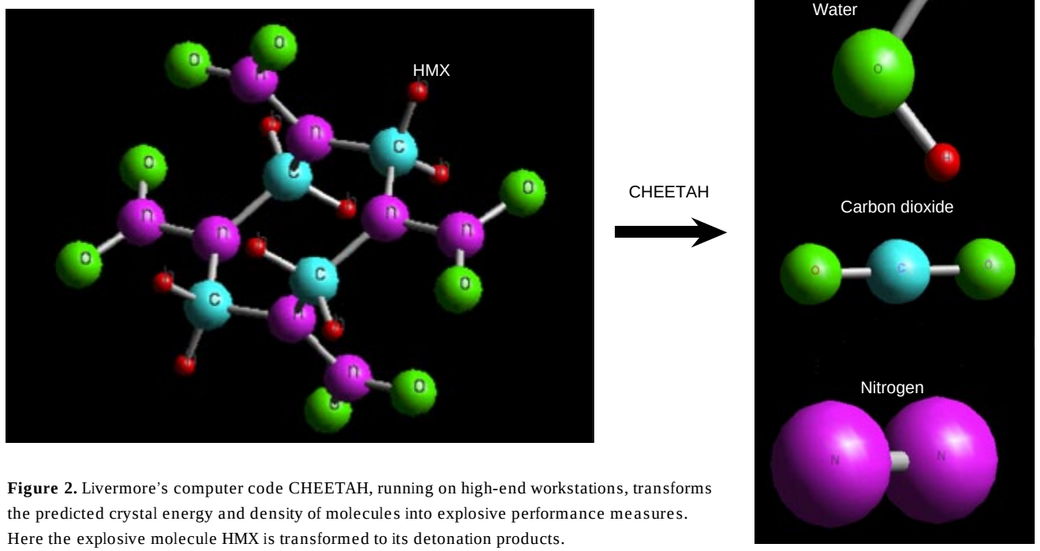


Figure 2. Livermore's computer code CHEETAH, running on high-end workstations, transforms the predicted crystal energy and density of molecules into explosive performance measures. Here the explosive molecule HMX is transformed to its detonation products.

HMX-based materials.* LX-19 is based on CL-20 (developed at the Naval Weapons Center, China Lake, California). Working with the Navy, Livermore experts determined many of the characteristics of CL-20 and performed the first scale-up to kilogram quantities at the Laboratory's Site 300 test area.

A similar effort is aimed at synthesizing materials with more energy than TNT, the best known high explosive in the world and one that offers less power (but better sensitivity) than HMX. For this effort, Livermore has synthesized LLM-105, an insensitive energetic material with 60% more energy than TNT. The new material is under evaluation by Ron Lee and his colleagues in Livermore's Defense and Nuclear Technologies Directorate.

In the process of developing new compounds and more efficient pathways for synthesizing existing compounds, the synthesis group has developed an innovative and cost-effective approach called the VNS (vicarious nucleophilic substitution) method for producing TATB. The procedure eliminates the need for chlorinated compounds, which have adverse environmental effects. (See the November 1996 *Science & Technology Review*, pp. 21–23.) Livermore and DOE's Pantex Plant recently began a four-year effort to apply the VNS method in order to establish a lower-cost industrial supply of TATB.

Once a few grams of a material have been synthesized, they are passed on to experimental chemists for a battery of safety tests (Figures 4 and 5). The tests determine the material's sensitivity to

Figure 3. Organic chemist Phil Pagoria synthesizes a new high-energetic compound inside a glovebox to guard against unwanted moisture.

Figure 4. Scientific Associate Chet Lee measures the burn rate of a high explosive under high pressure, a standard safety test.

Figure 5. Chemist Rosalind Swansiger remotely controls a performance test of a promising high explosive.

* Experimental molecules are designated by an LLM number for Lawrence Livermore molecule. Experimental formulations are designated by an RX number for research explosive. Once the material is in production, it acquires an LX designation for Livermore explosive. DoD experimental munitions receive an XM number.

impact, heat, friction, electrostatic discharge, and shock. Most candidate materials fail at this point. Those that pass are sent on to other chemists for incorporation in a mixture of ingredients called a formulation. Simpson acknowledges that the process is "still largely an art" but adds that it is becoming "more precisely scientific all the time."

A World of Tradeoffs

Formulating high explosives for unique applications may require a medley of ingredients, including energetic crystalline powders, energetic liquids, inorganic oxides, metals, and binders such as thermoplastics, thermosets, and gels. The binder, which takes up as little as 2% and as much as 40% of the volume, can serve several purposes: it can make the explosive easier to fabricate into useful shapes, aid in desensitization to shock, or modify the high explosive's performance characteristics.

Formulations chemist Mark Hoffman acknowledges the role of artistry in arriving at a sound formulation but notes that Livermore people can tap 45 years' worth of experience with high explosives. Much of the artistry is spent juggling the tradeoffs among sensitivity, performance, and cost. As a formulation increases insensitivity to explosion (for safety considerations, for example), performance typically suffers. Hoffman notes: "It does no good to have a weapon on board a tank that does not possess enough power to destroy or incapacitate an opposing tank. But it's inappropriate to carry a weapon that's so sensitive that it explodes in response to a few bumps in the road."

Formulators work closely with other chemists, who can quickly obtain safety and performance measurements using different quantities of a formulation. With as little as 1 to 2 grams, chemists can only perform critical safety tests. With 50-gram quantities, they can evaluate how well the ingredients of a formulation come together to form the new explosive. As formulations are scaled up to kilogram quantities, important tests of performance, thermal stability, and mechanical and physical properties assist designers in evaluating a formulation and determining appropriate use in specific devices. Chemical reactivity tests, for example, identify incompatibilities between device components and a formulation. Because a major objective in formulation is incorporation of the formulated explosive into a device, any possible incompatibility between device components and the formulation must be corrected early.

Atkins notes that obtaining accurate data from experiments at the extreme temperature, pressure, and time regimes of high explosives presents enormous challenges. Many of the tests use diagnostic tools originally developed for underground nuclear weapons tests at the Nevada Test Site. Others were developed more recently. One such tool is the multibeam Fabry–Perot velocimeter, designed by Livermore scientists (July 1996 *Science & Technology Review*, pp. 12–19). This device provides high-resolution, continuous velocity data about the behavior of materials traveling up to 3,000 meters per second. With the multibeam system now producing more meaningful data about the power of explosives—the rate at which they are capable of releasing energy—modeling codes become increasingly accurate. The device also allows more efficient use of budgeted funds because one experiment provides many sets of velocity data, thus taking the place of five separate experiments.

Computer simulations have also strengthened formulation activity and testing. CHEETAH is once again called into play, this time to suggest how the various formulation ingredients will affect performance. In addition, TOPAZCHEM-2D/3D, PALM, and more recently, the ALE3D code (see box, below) augment safety testing by predicting changes in thermal and chemical properties caused by different accident, battlefield, and aging scenarios.

Encouraging results from experiments and computer simulations lead to still

Spotlight on Safety

The very destructive power of high explosives places a premium on all aspects of their safety, including manufacture, transportation, storage, and handling. Likewise, much of Lawrence Livermore's high-explosives work involves determining the sensitivity of existing high explosives and rocket propellants to fire, accident, and terrorist attack.

Safety has also come under the purview of computer codes. "We would like to do predictions of safety at the start of the development process, much as we determine other characteristics of candidate molecules," says theoretical chemist Larry Fried, who is exploring using the widespread computer code GAUSSIAN to determine how much energy it takes to break a molecular bond as an indicator of sensitivity to accidental detonation. He is also exploring the conversion of intermolecular phonons (quanta of vibration energy) to intramolecular vibrational states as part of a computational model that could eliminate inherently unstable molecules from consideration before they are synthesized.

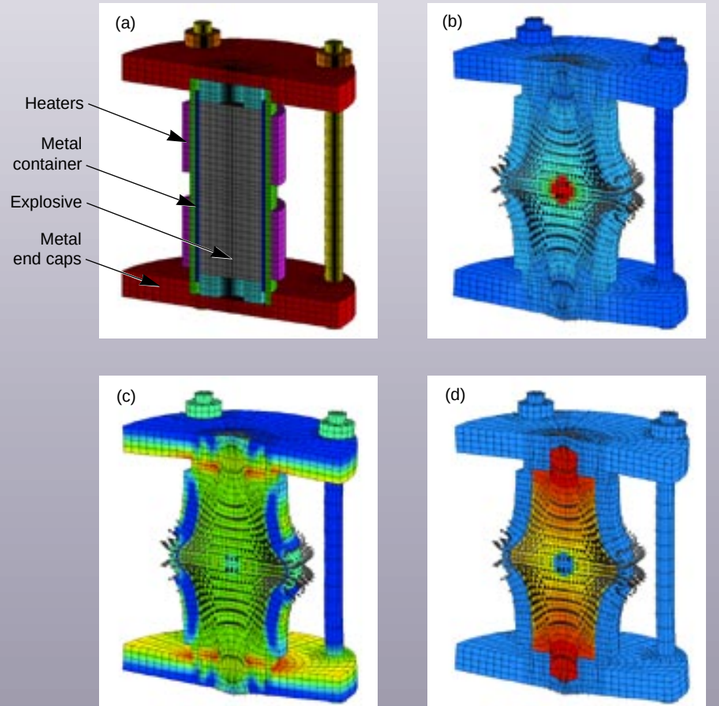
Fellow theoretical chemist Al Nichols has been working with computational scientists from the Defense and Nuclear Technologies Directorate to transform ALE3D, a three-dimensional hydrodynamic, explosive-safety code developed at Livermore (see figure on p. 11). With the ALE3D team, Nichols has added thermal and chemical capabilities to the code so it can answer safety questions about high explosives, in particular a stringent military thermal safety test called "cookoff." Thanks to ALE3D, Livermore is the first research center to simulate cookoff by depicting a remarkably wide time span. The code models deformations in a heated explosive device from the time they begin at the rate of millimeters per day to the instant of explosion when deformation rates increase to kilometers per second.

Safety efforts include working with the Air Force on its missile propellants. One study, a part of the Titan IV program, is looking at the safety ramifications of solid propellant falling from an errant rocket launch, as happened earlier this year when an Air Force Delta rocket blew up at Cape Canaveral, Florida, raining propellant down on the ground below. Another study concerns the propellants of the Air Force Minuteman III missile.

In performing the safety studies, says experimental chemical engineer Jon Maienschein, Livermore chemists are doing business differently by modeling every experiment before it is conducted. In that respect, says Energetic Materials Section leader Randy Simpson, Livermore scientists do a smaller number of experiments than are done at other sites, but they thoroughly instrument each one and precede major experiments with computer simulations.

Maienschein notes that Livermore personnel are working more closely with colleagues and sponsors in DoD. "Both they and we recognize that we can do more by teaming up with each other." The process, he says, encourages creative thinking about, for example, a new generation of transducer-based systems that continuously monitor important safety data such as temperature in high explosives.

Energetic Materials Center Director Ron Atkins notes that in a world of diminished federal outlays, collaboration is clearly the way to achieve important advances with the greatest cost-efficiency. "We're working hard to build bridges to the armed services, DOE centers like the Pantex Plant in Texas, and other national labs," he says.



The ALE3D computer code is capable of simulating a "cookoff" safety test by modeling the rate of deformations in a slowly heated high explosive over a wide time span. (a) A model of the test at setup. The high explosive is encased in steel and aluminum and bolted between two metal end caps. Heaters surround the metal container and heat the 7.6-centimeter-tall device at the rate of 3.3°C per hour. (b), (c), and (d) are snapshots of the simulation of the material's deformation as a function of (respectively) temperature, pressure, and chemical change after 50 hours of heating. ALE3D simulations such as this tell energetic-materials scientists in great detail and in slow motion how, when, and with what violence new high-explosive compounds deform when burned. In (b), (c), and (d), the velocity of deformation is 80 meters per second.

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larger-scale formulations of 400 grams or greater done at Site 300. When the material properties are optimized, the formulation process is developed for scale-up to production quantities for final technology transfer.

Livermore chemists are also working to improve efficiencies in the production world. They are exploring the use of injection molding equipment much like that used to make plastic toy parts. Such machines could be ideal for making shaped charges, which typically contain a number of complex folds that are difficult to fashion using standard production machinery (Figure 6).

Leaving the Iron Age

Simpson describes the Iron Age as a time when builders were limited to a few metals for construction. Now builders have a host of different materials from which to choose. "We're leaving the Iron Age of energetic materials because military planners are no longer limited to TNT and HMX," he says. "We're seeing specific new materials for specific military applications."

The driving force is the ascendancy of smart munitions. Because these weapons routinely hit their targets, small improvements in the lethality of the warheads can significantly increase their effectiveness. What's more, fewer and smaller munitions mean that more expensive energetic materials may be used.

As part of this new effort, Livermore chemists are working with the Navy to adapt LX-19 and similar CL-20 formulations to the military's XM-80 program. Multiple small submunitions, each containing about 10 grams of explosives, will be grouped in shells and shot out of Navy guns. Capable of traveling long distances, the shells, which have a propulsion system guided by global positioning satellites, will accurately destroy enemy fortifications.

Simpson is confident that computer codes will continue to become more sophisticated so that a code such as ALE3D will be used as a design tool to model safety elements of energetic devices as diverse as rockets or automobile air bags. It is a safe bet that with other aspects of high explosives, as well, Livermore researchers will play a large part in the new age of high explosives.

—Arnie Heller

Figure 6. At Site 300 facilities, injection-moldable explosives are developed as part of an effort to enhance production methods. (a) Mark Hoffman formulates a moldable high explosive. (b) Hoffman and Kirk Pederson pour the explosive to a transfer funnel, from which it is poured into a deaerator–loader. (c) Frank Garcia operates the deaerator–loader to remove air from the explosive before loading it into the explosive device. (d) Mike Kumpf displays the finished precision explosive device.

Key Words: ALE3D, CHEETAH, Fabry–Perot velocimeter, GAUSSIAN, high explosives, High Explosives Applications Facility (HEAF), HMX (cyclo-tetramethylene-tetranitramine), MOLPAK, PALM, stockpile stewardship, TATB (triamino-trinitrobenzene), TNT (trinitrotoluene), TOPAZCHEM.

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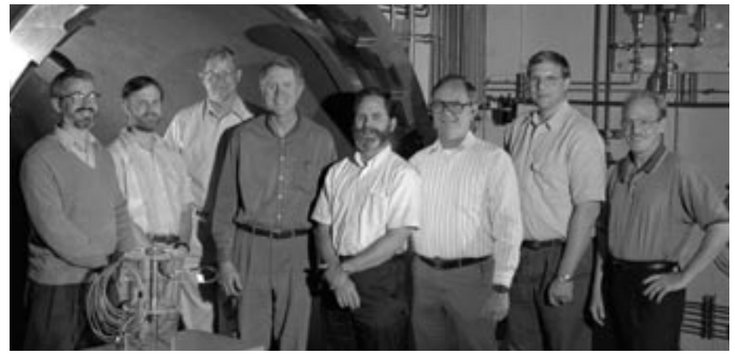
About the Scientists



The research, development, and testing of new energetic materials done at the Laboratory's High Explosives Applications Facility is, like all science done at Livermore, a multidisciplinary team effort. In this instance, the team members operate under the auspices of the Energetic Materials Center (EMC), sponsored jointly by Lawrence Livermore and Sandia national laboratories. Chief contributors to the new science of high explosives being done at Livermore are (left to right): ALBERT NICHOLS, a theoretical chemist currently working to model safety aspects of high explosives used in nuclear and defense applications; RANDALL SIMPSON, an experimental chemist who develops new energetic materials and characterizes their initiation and detonation properties; RONALD ATKINS, director of the EMC and coordinator of the team's work; RONALD LEE, a physicist who develops new explosive initiation systems; JON MAIENSCHEIN, an experimental chemical engineer involved in computer simulations of the safety of energetic materials before their testing; MARK HOFFMAN, a formulations chemist responsible for formulating high explosives for unique applications within strict safety, performance, and compatibility guidelines; LAWRENCE FRIED, a theoretical chemist who screens candidate high-explosives molecules using advanced computer codes; and PHILIP PAGORIA, an organic chemist, who is expert in synthesizing new high-energetic compounds.