Science & Technology REVIEW

June 2001

U.S. Department of Energy's
Lawrence Livermore
National Laboratory

Carbon Conversion
A Source of Clean Electricity

Also in this issue:

- **California Environmental Research Has Broad Applications**
- **Nitrogen Fullerenes Are Potential Powerhouse**
- **PEREGRINE Gets the Go-Ahead**

About the Cover

Lawrence Livermore scientists are working on numerously environmentally friendly technologies to help meet the long-term energy needs of the U.S. One of these—the direct carbon conversion fuel cell—is the subject of this month's feature article beginning on p. 4. The cover shows a microscopic view of one of the "turbostratic" carbon materials that make it possible for the carbon conversion fuel cell to efficiently produce clean electricity directly from carbons derived from fossil fuel. During the past year, Livermore scientists have convincingly demonstrated the direct carbon conversion process in the laboratory and are at work optimizing the design of the fuel cell that will make the process a practical, cost-effective alternative source of electric power.

Cover design: Lew Reed

About the Review

Lawrence Livermore National Laboratory is operated by the University of California for the Department of Energy. At Livermore, we focus science and technology on assuring our nation's security. We also apply that expertise to solve other important national problems in energy, bioscience, and the environment. *Science & Technology Review* is published 10 times a year to communicate, to a broad audience, the Laboratory's scientific and technological accomplishments in fulfilling its primary missions. The publication's goal is to help readers understand these accomplishments and appreciate their value to the individual citizen, the nation, and the world.

Please address any correspondence (including name and address changes) to *S&TR*, Mail Stop L-664, Lawrence Livermore National Laboratory, P.O. Box 808, Livermore, California 94551, or telephone (925) 423-3432. Our e-mail address is str-mail@llnl.gov. *S&TR* is available on the World Wide Web at www.llnl.gov/str/.

Prepared by **LLNL** under contract No. W-7405-Eng-48

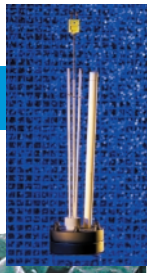
Science & Technology REVIEW

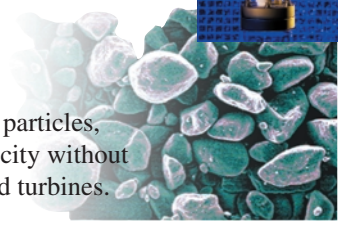
June 2001

Lawrence Livermore National Laboratory

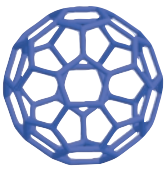
Contents

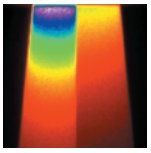
Features





Research Highlights





Departments

S&TR Staff

S&TR, a Director's Office publication, is produced by the Technical Information Department under the direction of the Office of Policy, Planning, and Special Studies.

S&TR is available on the Web at www.llnl.gov/str/.

Printed in the United States of America

Available from
National Technical Information Service
U.S. Department of Commerce
5285 Port Royal Road
Springfield, Virginia 22161

UCRL-52000-01-6
Distribution Category UC-0
June 2001

Coating protects, improves telescopes

Livermore scientists Jesse Wolfe and Norman Thomas have patented an ultrathin silver coating for mirrors that is far more durable than any previously used. It improves the long-term performance of telescopes and lasers by slowing the deterioration of the mirror coatings vital to these instruments.

Wolfe, Thomas, and their support team recently coated a 56-centimeter-diameter mirror at the Keck Observatory in Hawaii. Within the next few months, the mirror coating is also scheduled for installation on several of the world's major telescopes, including Kitt Peak in Tucson, Arizona, and possibly the South African Large Telescope and the California Extremely Large Telescope.

Thomas explains, "These large telescopes typically involve five or six reflections from coated mirrors, which affect the collection efficiency. Our coating will give each mirror a consistent 97-percent reflectivity. Previous coatings provided about 90-percent reflectivity. Combine the effect from several mirrors, and we may have up to 35-percent increased collection efficiency for many years from each of these large telescopes."

The improved coating is also being installed to protect the thousands of mirrors to be used in the National Ignition Facility's (NIF) flashlamps, according to Wolfe. Research on the more durable coating was initiated for the NIF project.

In June, mirrors with the new silver coating will travel to the International Space Station for long-term testing in the rigorous conditions of outer space.

Contact: Norman Thomas (925) 422-0486 (thomas19@llnl.gov).

Teller Education Center founded for K–12 teachers

The University of California at Davis, in collaboration with the UC Office of the President, UC Merced, and Lawrence Livermore National Laboratory, has established the Edward Teller Education Center adjacent to the UC Davis Department of Applied Science at Livermore.

Funded by the Office of the President and the Laboratory, the center will provide opportunities for the professional development of kindergarten-through-twelvth-grade (K–12) teachers working in participating school districts within the Tri-Valley area surrounding the Laboratory and the San Joaquin and Sacramento valleys in central California. In addition, local community colleges and school districts, state universities, and industry will support and participate in center activities. The center will provide learning opportunities to support professional development throughout a teacher's career. It may also offer advanced-placement science classes for students who otherwise would not have access to them.

The new 338-square-meter building includes a wet laboratory classroom, a computer technology classroom, high-speed computer network connections, and overhead projection systems to demonstrate the latest teaching tools and instruction methods. The facility is scheduled to open September 1, 2001.

The center is named for Edward Teller, co-founder of Lawrence Livermore, the founding chair of the Department of Applied Science at UC Davis, and a life-long promoter of excellence in science education.

"The center is a fantastic resource to help teachers from various disciplines develop their teaching skills and acquire content knowledge," says Richard Farnsworth, interim director of the center and manager of K–12 education and outreach for Livermore's Science and Technology Education Program.

Contact: Richard Farnsworth (925) 422-5059 (farnsworth1@llnl.gov).

Prototype EUVL chip-making machine unveiled

In early April at Sandia National Laboratories in Livermore, California, industry and government officials celebrated the completion of the first full-scale prototype machine for making computer chips using extreme ultraviolet lithography. EUVL technology is a breakthrough that will lead to microprocessors that are tens of times faster than today's most powerful chips and create memory chips with similar increases in storage capacity.

"The completion of the prototype machine marks a major milestone for the program, since we have proven that EUV lithography works," says Chuck Gwyn, program manager of the Extreme Ultraviolet Limited Liability Company (EUV LLC), the consortium of Intel, Motorola, Advanced Micro Devices, Micron Technology, Infineon, and IBM.

Through an agreement that spans 1997 through early 2002, EUV LLC is funding the EUVL development research by the Virtual National Laboratory (VNL), a collaboration of three Department of Energy national laboratories—Lawrence Livermore, Lawrence Berkeley, and Sandia. The VNL–EUV LLC collaboration produced the prototype EUVL machine, called the Engineering Test Stand.

At the April celebration, John Gordon, administrator of the DOE's National Nuclear Security Administration, asserted, "The EUVL partnership demonstrates that fundamental science and innovative ideas can be applied toward solutions in both the commercial and public sectors. These kinds of challenges are exactly the kind of work our national laboratories does best."

Contact: Gordon Yano (925) 423-3117 (yano1@llnl.gov).

Addressing the Energy–Environment Challenge

CALIFORNIA'S current energy crisis has put energy issues onto the front page again. Our society's immediate concerns have focused on ensuring adequate power supplies, avoiding rolling blackouts, and reducing stratospheric energy bills. At the same time, a growing number of people have cited the environmental and public health consequences of unfettered energy consumption. The rising debate over the environmental aspects of the energy crisis has many elements, including the buildup of greenhouse gases, the recent Kyoto accords on limiting nations' atmospheric emissions, spills and leakage of fuels, and the general environmental degradation associated with extracting and transporting our energy resources.

The events, discussions, and debates of the past few months have again vividly demonstrated that the nation wants energy that is cheap, reliable, and clean. We do not want to be forced to choose between having adequate energy supplies and enjoying a healthy environment.

Clearly, one of the nation's most pressing challenges is solving our energy needs while lessening the environmental effects of energy production and consumption. Several trends have emerged that are leading to a national mandate to address the coupled energy–environment issue. These trends include the increasingly strong evidence of climate change, a continuing reliance on fossil fuels, the unrelenting U.S. energy appetite, the possibility that the developing world will dramatically increase its consumption of fossil fuel, and growing international pressures on the U.S. to curb its carbon dioxide emissions.

Lawrence Livermore possesses a wide range of technical assets that position us to comprehensively address the energy–environment issue. They include the Program for Climate Model Diagnosis and Intercomparison, the development of carbon-sensitive energy production and conversion technologies, carbon-cycle and climate simulation, terascale computer hardware and expertise, and expert knowledge in risk assessment and decision support. Together, these assets provide a deep understanding of the energy–environment issue as well as innovative energy and environmental remediation technologies to address the issue.

The recent merger of Lawrence Livermore's Energy Directorate and Earth and Environmental Sciences Directorate into the Energy and Environment Directorate has enhanced the Laboratory's capabilities to combine traditional lines of research in energy and in climate. In that light, Livermore scientists are pursuing several integrated initiatives to advance scientific understanding of the energy–environment issue. The initiatives include integrated climate and carbon-cycle prediction, a zero-emission steam technology research facility, solid-oxide fuel-cell technology development, methane-hydrate risks and opportunities assessment, and carbon sequestration in the ocean or subsurface.

One of the most promising long-term technology options is direct carbon conversion, featured in the article beginning on p. 4. Future energy technologies must be cost-effective, meaning that the technologies must be modular and scalable and not as capital intensive as previous technologies. They must also be clean and efficient to minimize injury to the environment and facilitate the mitigation of carbon dioxide emissions.

Direct carbon conversion fuel cells offer the potential to be economical, clean, and efficient while using the vast fossil energy resources of oil, coal, natural gas, and biomass. The technology offers high electrochemical efficiency with the added advantage of controlled emission of carbon dioxide that can be disposed of in an environmentally acceptable way. It is a breakthrough based on a new understanding of how to use carbon fuel particles that are extremely small and have a high degree of disorder on the atomic scale.

Many challenges remain to be overcome, including how to use dirty fuels, scaling up the technology to significant size, and performing thorough systems engineering. Nevertheless, direct carbon conversion is a promising candidate for the nation's energy future.

■ Lee Younker is Associate Deputy Director for Science and Technology.

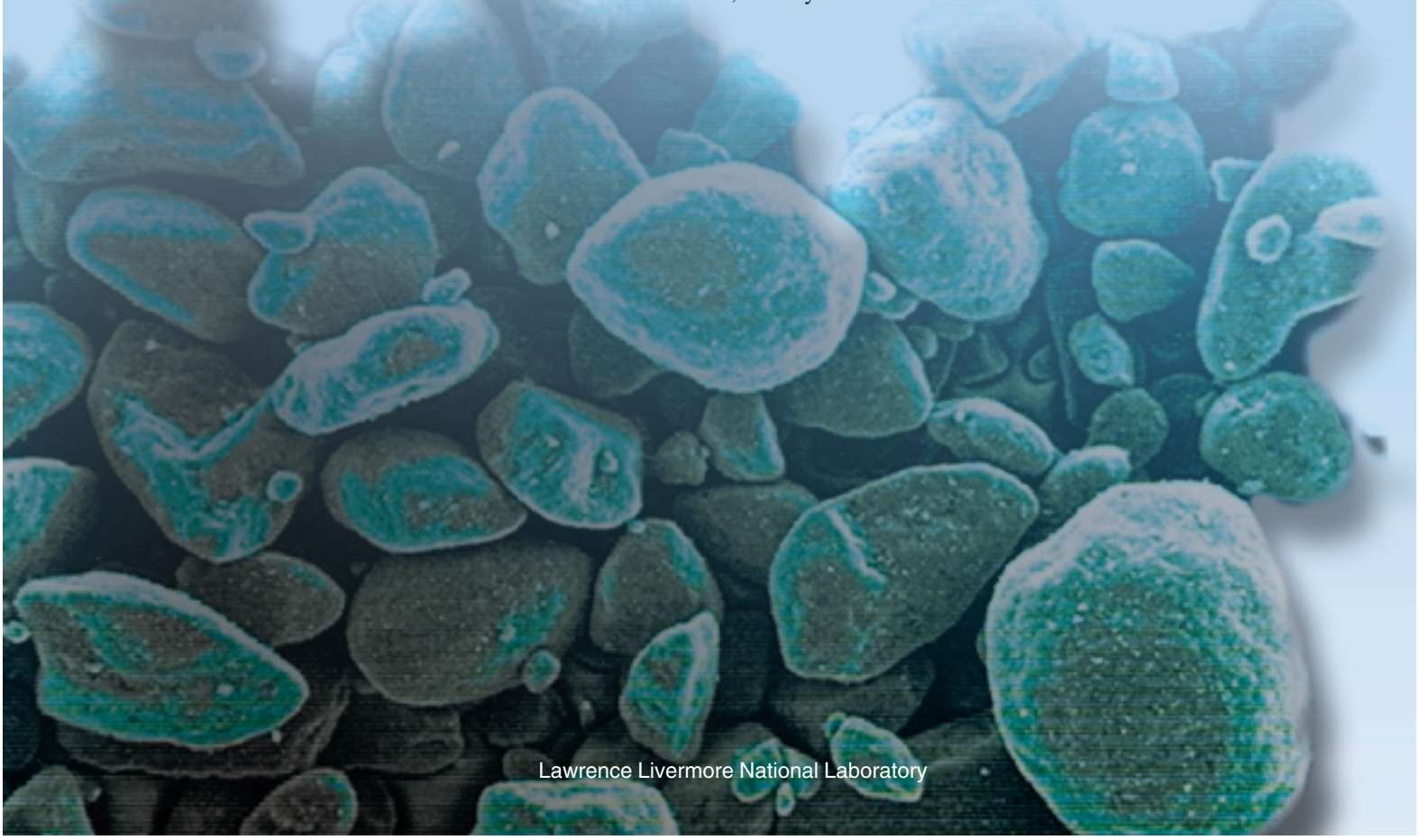
Turning Carbon Directly into Electricity

The carbon conversion fuel cell pushes the efficiency of using fossil fuels to generate electricity closer to theoretical limits.

THE long-term energy—and environmental—future of the United States is much in the headlines these days. Helping to make the prospects brighter is a team of Lawrence Livermore scientists working to develop a method for producing electricity that is safe, relatively simple, remarkably efficient, and kind to the environment.

Called direct carbon conversion, the process has been demonstrated convincingly in the laboratory over the past year. The electrochemical process converts carbon particles, obtained from different fossil fuels, directly into electricity without the need for such traditional equipment as steam-reforming reactors, boilers, and turbines.

The breakthrough Lawrence Livermore method, the result of a two-year study funded by the Laboratory Directed Research and Development Program, pushes the efficiency of using fossil fuels for generating electricity far closer to theoretical limits than ever before. If adopted on a large scale, direct carbon conversion would help to conserve precious fossil resources by allowing more power to be harnessed from the same amount of fuel. It would



Lawrence Livermore National Laboratory

also improve the environment by substantially decreasing the amount of pollutants emitted into the atmosphere per kilowatt-hour of electrical energy that is generated. Perhaps most important, it would decrease emissions of carbon dioxide, which are largely responsible for global warming.

"What if we could nearly double the energy conversion efficiency of fossil fuels in electric power generation over the conversion efficiency of today's coal-fired power plants—which is about 40 percent—and thereby cut the carbon dioxide emissions per kilowatt almost in half?" asks lead researcher John Cooper, scientific capability leader for electrochemistry and corrosion in Lawrence Livermore's Chemistry and Materials Science Directorate. "And what if we could produce a pure carbon dioxide byproduct for sequestration or industrial use at no additional cost of separation while avoiding the air pollution problems associated with combustion?"

Cooper explains that direct carbon conversion requires a unique kind of fuel cell. A fuel cell is an electrochemical device that efficiently converts a fuel's chemical energy directly to electrical energy without burning the fuel. However, instead of using gaseous fuels, as is typically done, the new technology uses aggregates of extremely fine (10- to 1,000-nanometer-diameter) carbon particles distributed in a mixture of molten lithium, sodium, or potassium carbonate at a temperature of 750 to 850°C. The overall cell reaction is carbon and oxygen (from ambient air) forming carbon dioxide and electricity.

The reaction yields 80 percent of the carbon–oxygen combustion energy as electricity. It provides up to 1 kilowatt of power per square meter of cell surface area—a rate sufficiently high for practical applications. Yet no burning of the carbon takes place.

No Water to Boil

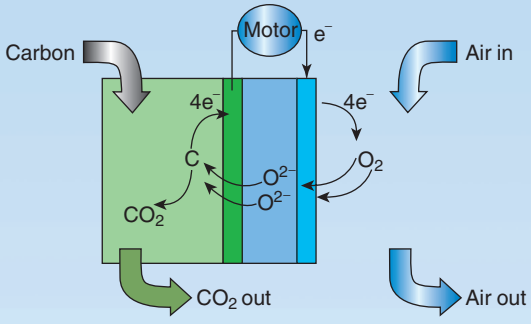
"We're not burning fossil fuels to boil water to drive turbines and dynamos to generate electricity," says Lawrence Livermore electrochemist Nerine Cherepy, who has been researching the breakthrough concept. "This is a simpler, more efficient, and more environmentally friendly process that obtains the greatest possible fraction of energy from the starting fossil fuel with little waste heat."

The thermodynamic efficiency of the direct carbon conversion cell exceeds the 70-percent requirement of the next-generation fuel cell envisioned by the Department of Energy. In contrast, conventional coal- and natural-gas-fired power plants are typically between 35- and 40-percent efficient. Combined-cycle pilot plants that burn natural gas in multistage turbines now operate at 57-percent efficiency, based on the higher heating value of the fuel. (Higher heating value, or HHV, is the total amount of heat released when a fuel is burned completely and the products are returned to their natural, room-temperature states.) High-temperature fuel cell hybrid systems (fuel cells combined with turbines), such as a technology developed by Westinghouse, are expected to operate on natural gas at 60-percent HHV.

Direct carbon conversion can use fuel derived from many different sources, including coal, lignite, petroleum, natural gas, and even biomass (peat, rice hulls, corn husks). Cooper notes that 90 percent of Earth's electric energy comes from the burning of fossil fuels. Half of our fossil-fuel resources is coal, and 80 percent of the coal belongs to the United States and Canada, the former Soviet Union, and China. Coal-fired plants produce 55 percent of U.S. electricity—as well as large amounts of pollutants. As a result, the vast energy reserves of coal remain underused. Direct carbon conversion has the potential to be the long-sought "clean coal" technology.

The carbon–air fuel cell gives off a pure stream of carbon dioxide that can be captured without incurring additional costs of collection and separation from smokestack exhausts. The stream of carbon dioxide, already only a fraction of current processes, can be sequestered or used for oil and gas recovery through existing pipelines. (Lawrence Livermore environmental scientists are studying the sequestering of carbon dioxide in geologic formations as part of a Department of Energy effort. See *S&TR*, December 2000, pp. 21–23.)

Pyrolysis—the thermal decomposition method used to turn hydrocarbons into hydrogen and tiny pure carbon particles



Carbon (C) and oxygen (O_2) can react in a high-temperature fuel cell with the carbon, delivering electrons (e) to an external circuit that can power a motor. The net electrochemical reaction—carbon and oxygen forming carbon dioxide—is the same as the chemical reaction for carbon combustion, but it allows greater efficiency for electricity production. The pure carbon dioxide (CO_2) product can be sequestered in an underground reservoir or used to displace underground deposits of oil and gas.

used in direct carbon conversion—consumes less energy and requires less capital than the electrolysis or steam-reforming processes required to produce hydrogen-rich fuels. Pyrolysis produces billions of kilograms of carbon blacks annually in the U.S. Carbon black is a disordered form of carbon produced by thermal or oxidative decomposition of hydrocarbons and is used to manufacture many different products, including tires, inks, and plastic fillers.

Old Dream

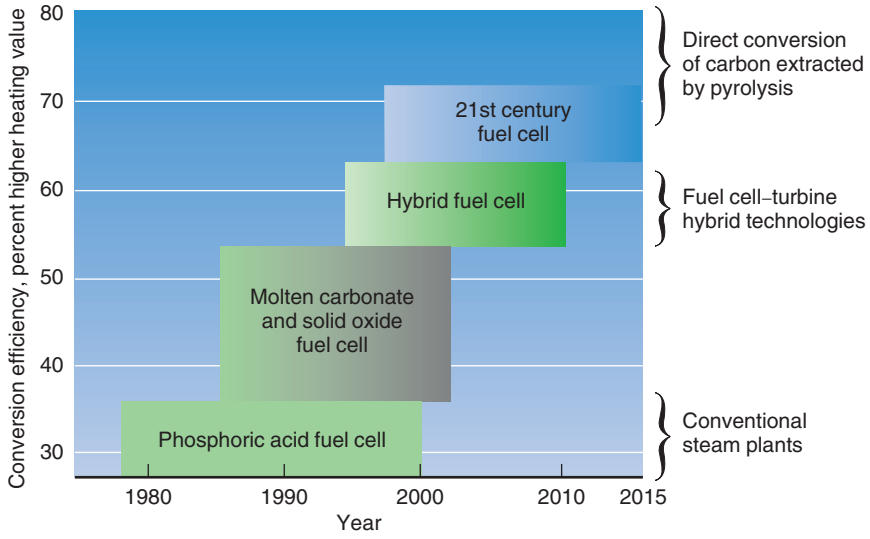
Electricity direct from coal is one of the earliest dreams of electrochemical science. The first attempts date from the late 19th century, when Boston entrepreneur William Jacques fashioned a coal fuel battery that used coke electrodes in a molten sodium hydroxide electrolyte. Because the molten electrolyte became exhausted, Jacques's invention operated as an exhaustible battery, not as a fuel cell, despite impressive demonstrations on the kilowatt scale. Other problems included a buildup of ash entrained with the fuel, the cost of making the carbon anodes, and the difficulty of distributing carbon fuel electrodes to the many cells. Efforts to develop practical carbon-based fuel cells during the 20th century, such as those tested at the Stanford Research Institute in the 1980s, were also hindered by the buildup of ash and by the costs and difficulties of carbon electrode manufacture.

The Lawrence Livermore approach circumvents the historic barriers to a coal fuel cell by using extremely fine, virtually ash-free, "turbostratic" carbon particles that contain small amounts of ash and have a high degree of structural disorder on the nanometer scale. The team found that turbostratic carbon particles, when mixed with molten carbonate to form a slurry, operate like rigid electrodes when the melt is brought into contact with an inert metallic screen. Exactly how the carbon particle delivers energy to the screen is under investigation, but reactive chemicals in the melt produced by the carbon are likely intermediates.

Also, the team found that carbon particles can be distributed pneumatically to individual cells by a small amount of carbon dioxide fed back to the cell from the continuously produced carbon dioxide stream. (The pneumatic transport of carbon particles through complex equipment is a widespread industrial practice.)

The carbon particles and oxygen (ambient air) are introduced as fuel and oxidizer, respectively. The slurry formed by mixing carbon particles with molten carbonate constitutes the anode. The anode reaction is carbon and carbonate ions forming carbon dioxide and electrons. At the cathode, which is similar to that used in other high-temperature fuel cells, oxygen, carbon dioxide, and electrons from the anode form carbonate ions. A porous ceramic separator holds the melt in place and allows the carbonate ions to migrate between the two compartments.

The technology has been demonstrated in a number of small, experimental cells with reaction areas of about 3 to 60 square centimeters. The cells feature different designs and different materials, including stainless steel, ceramic, and sometimes graphite. Each cell type features tubes for gases to enter and exit the cell, thermocouples (for measuring temperature), and a reference electrode. Temperature is maintained by a



Various kinds of fuel cells using phosphoric acid, molten carbonate, and solid oxide yield electricity from methane fuel at efficiencies in the range of 35 to 55 percent of higher heating value. Using waste heat from the fuel cell in turbines (hybrids) can increase the total efficiency even further. The thermodynamic efficiency of the direct carbon conversion cell already exceeds the 70-percent efficiency goal of the 21st century fuel cell envisioned by the Department of Energy.

computer-controlled furnace. The computer also acquires continuous data on current and voltage.

In repeated tests, the cells deliver up to 0.1 watt continuously per square centimeter and are 80-percent efficient at 80 milliwatts per centimeter. Recently, using a new cell design that automatically regulates the amount of molten salt, the team has operated cells for days, simply by adding more carbon fuel.

Doubly Attractive

The carbon–oxygen reaction is attractive in two unique ways, says Cooper. First, almost no entropy change occurs in the overall cell reaction. (Entropy is a measure of the disorder in a system. A significant entropy decrease would mean that the cell produces a great deal of waste heat.) Because the entropy change is close to zero for the carbon–oxygen reaction, 100 percent of the heat energy of combustion of the carbon can instead be converted by the cell into electrical energy under ideal conditions.

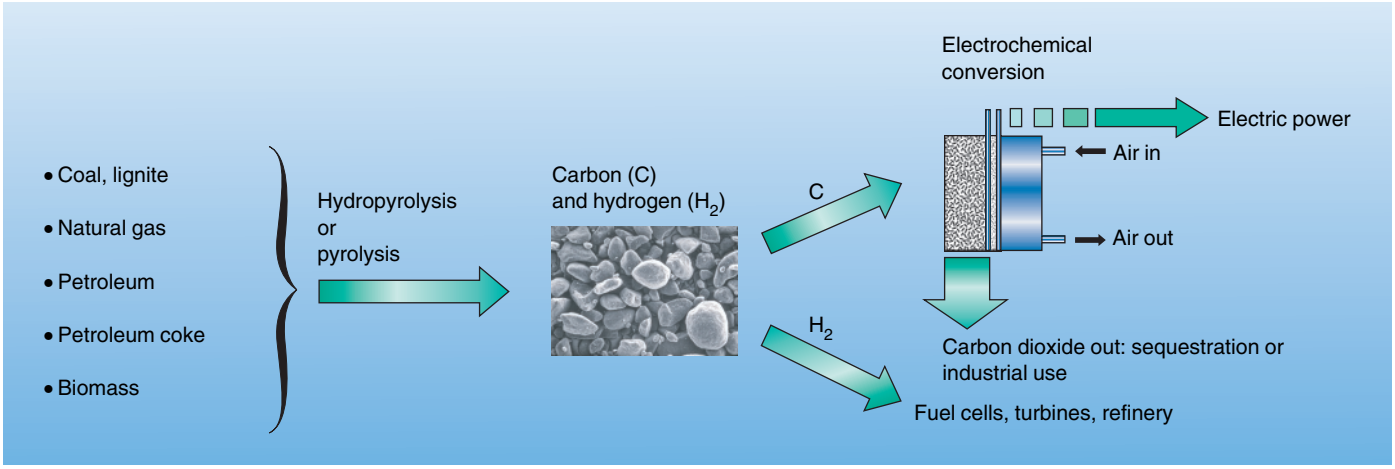
Second, the driving force for energy production, called electromotive force or maximum voltage, does not degrade as the carbon is progressively consumed to make power and carbon dioxide, so the voltage remains constant.That means that in making a single pass through the cell, all the carbon is consumed at a maximum yet constant voltage.

"Realistically, we can get out a maximum of about 80- to 85-percent efficiency, based on the heating value of the carbon, when the cell is operated at a practical rate, which is about 100 milliamperes per square centimeter," says Cooper. "The losses are primarily those associated with the sluggishness of electrode reactions and the electrical resistance of the cell. It was the two thermodynamic properties—zero entropy change and constant electromotive force—that first drew our attention to carbon as an attractive electrochemical fuel." In contrast, the entropy decrease for the hydrogen–oxygen reaction in high-temperature fuel cells limits conversion efficiency to 70 percent of the fuel's HHV, while electrical efficiencies (about 80 percent) and practical fuel use (about 80 percent) further reduce the total efficiency to below 50 percent. (See the box on p. 10.)

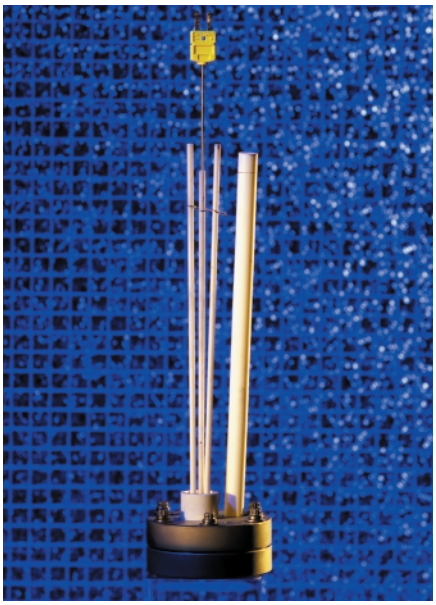
The part of a fuel's combustion energy that is not converted to electric power appears as heat. Some of this heat could be used to generate steam and drive a turbine generator, as in hybrid systems. But the additional cost and complexity must be weighed against the comparatively small additional savings in fuel.

Nanostructure Is Important

Cherepy and senior scientific associate Roger Krueger have tested a number of pure carbons that differ principally in the degree and nature of disorder on the nanoscale. They have correlated significant differences in the carbon fuels' three-dimensional atomic structures with their electrochemical reactivities. The more disordered the carbon atoms, the more easily they yield electrons. Cherepy and Krueger are paying particular attention to turbostratic carbons, which feature planes of atoms arranged at different angles and with lots of defects at the edges that make the atoms more accessible for chemical reactions. (Graphite, in contrast, has a more ordered structure and is less reactive by a factor of about 1,000.)



In principle, any fossil fuel or biomass can be converted to electric power using direct carbon conversion. For natural gas and oil, pyrolysis (thermal decomposition) yields hydrogen and carbon. For dirtier resources (coals, biomass), the carbon may have to be extracted by reaction with hydrogen, followed by pyrolysis.



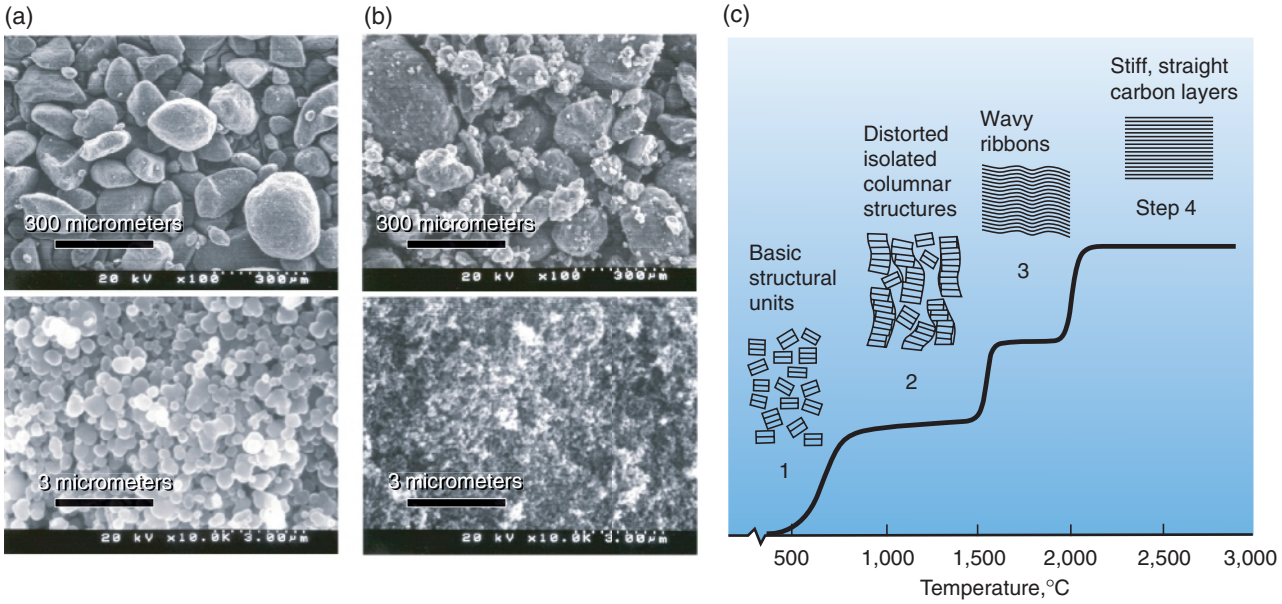
Simple cells in the laboratory are used to react carbon and atmospheric oxygen. These cells consist of a metal anode current collector, a ceramic matrix for holding the melt, and a metal screen for reacting the oxygen from the air.

Those candidate turbostratic carbons exhibiting discharge rates of more than 20 milliamperes per square centimeter at 0.8 volts have been analyzed in greater detail with transmission electron microscopy and x-ray diffraction. Researchers in Livermore's Chemistry and Materials Science Directorate conducted some of these characterization tests, and other characterizations have been done by Kim Kinoshita and coworkers at Lawrence Berkeley National Laboratory.

Cherepy's investigation has focused largely on carbon blacks because they have the highest electrochemical reactivity of any carbon fuel yet tested. Made from a variety of sources, carbon blacks are the basis of a large commercial industry. Four and a half billion kilograms per year of carbon black (all turbostratic to various degrees) are produced annually for automobile tires, pigments, plastics fillers, wire insulation, and other products. Although most carbon blacks contain about 0.02 to 0.05 percent residual ash, it should have no effect on system performance, cost, or cell lifespan because the rate of ash accumulation would be slow. (Carbon with 0.02-percent ash would clog the cell after about 50 years, five times the life expectancy of cell hardware.)

Among carbon blacks, a range of reactivities has been measured. For example, one carbon material had a peak power density of about 8 milliwatts per square centimeter while a second material measured almost 50 milliwatts per square centimeter. A third, the best material tested, yields energy at about 100 milliwatts per square centimeter and 100 milliamperes at 0.8 volts, sufficient for many fuel cell or battery applications.

Significant differences in microstructure and nanostructure were found in electron micrographs of the three samples, although all are nearly



The structure of the carbon material is the key to widely different electrochemical reactivities. The two carbon blacks in (a) and (b), revealed in photomicrographs at two magnifications, were produced by pyrolysis at different temperatures and started out as different fossil fuels. In (c), the degree of disorder of the carbon increases as the temperature of formation decreases from 2,000°C down to about 700 to 1,000°C.

pure carbon and look like black dusts. X-ray diffraction measurements showed that all had much greater spacing between layers of carbon atoms than does graphite. The x-ray data also revealed only small areas of crystallinity compared to graphite. Finally, the more reactive carbons have higher surface area and were found to oxidize more rapidly when exposed to high temperatures in air.

Cooper notes that the team is working to achieve a better understanding of the relationship between the nanostructure of carbons and their electrochemical reactivity in molten salts. A related goal is being able to predict carbon nanostructure from the conditions of pyrolysis and the nature of the starting materials undergoing pyrolysis. "Success here is critical to the economic attractiveness of the process and its ability to draw upon any fossil fuel resource," he says.

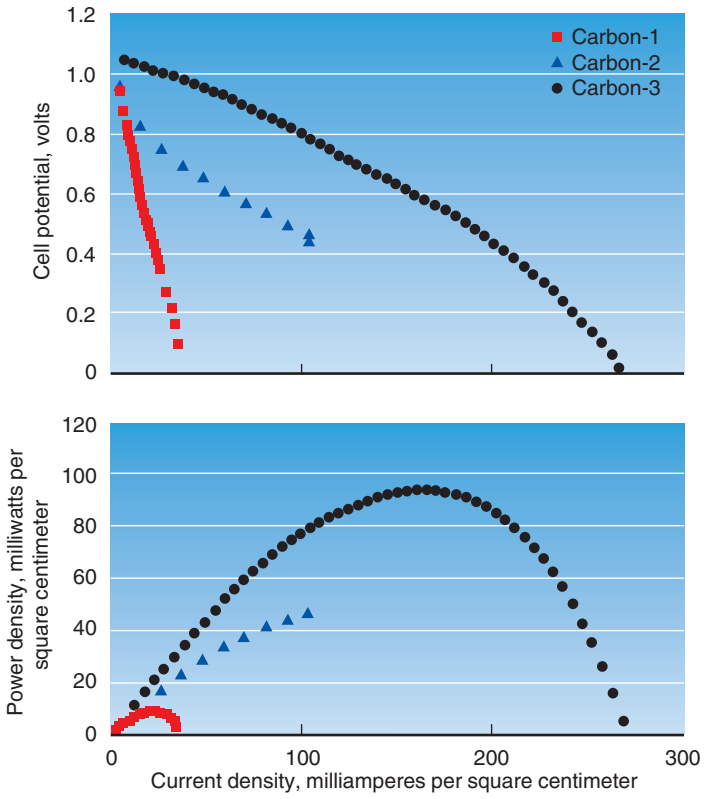
One Class of Fuels, Many Sources

A significant advantage of direct carbon conversion is that practically any fossil fuel, including coal, lignite, biomass, natural gas, and petroleum, can produce turbostratic carbons. One method, pyrolysis, uses moderate temperatures (800 to 1,200°C) to produce a stream of elemental carbon particles and a stream of hydrogen gas from a pure hydrocarbon. The byproduct hydrogen gas can be sold for a number of uses, including chemical synthesis, combustion, and powering fuel cells. The pyrolysis step consumes 5 to 10 percent of the starting fuel value (1 to 2 percent is lost because of process inefficiencies). Some fossil fuels, such as coal and biomass, first require treatment with hydrogen under high pressure to produce a hydrocarbon that can then be pyrolyzed into carbon fuel and recyclable hydrogen. This treatment is called hydropyrolysis and has many variants.

One of the most intriguing options is using coal as a carbon source because of the nation's (and the world's) vast resources of coal and the difficulty in using coal as a clean energy source. Because of most coal's high sulfur and ash content, it must undergo hydropyrolysis or some other means of purification.

Turbostratic carbon from petroleum coke could be highly advantageous for the carbon conversion cell, says Cooper, because it would likely be the least expensive source of carbon fuel. Some 2 to 8 percent of all petroleum refining ends up as petroleum coke, an inexpensive waste product that is naturally turbostratic and could be modified and used for direct carbon conversion. The amount of coke produced will increase as lighter crude resources become exhausted. Because coke commonly contains 0.25- to 5-percent sulfur, direct carbon conversion cells would require either coke refining or the use of graphite conductors in the carbon–air cell to prevent sulfur corrosion.

For natural gas, Cooper envisions small (100-kilowatt), transportable



Three carbon blacks are equally pure, are made by pyrolysis, and cost about the same, but they differ significantly in structure on the nanometer scale. As a result, their electrochemical reactivities are quite different. The two graphs depict the three carbons' voltage and power—two different functions of electrical current—as tested in a direct carbon conversion cell. Power densities (bottom) show carbon-3 reacting at a rate 10 times greater than carbon-1, providing about 100 milliwatts per square centimeter at 850°C. (Graphite, by comparison, is about 1,000 times less reactive than carbon-3.)

power stations that could be run from any natural gas pipeline. Such small power stations would be ideal in natural gas production fields; when a field becomes exhausted, the cell would be moved to a new location. Natural gas would be filtered and pyrolyzed at the wellhead. The resulting turbostratic carbon would go immediately to a direct carbon conversion cell, the hydrogen to a fuel cell, and hot carbon dioxide from the carbon cell used to displace more natural gas.

Direct carbon conversion might also make use of a significantly underused family of fuels that includes biomass, lignite, peat, and others. Some of this material, such as rice hulls, straw, and corn stalks, is simply burned in the field after harvest. Antipollution regulations are increasingly making such burning unlawful. Instead, such material could be charred, and the carbon component extracted with hydropyrolysis.

In analyzing the various fuel options, the team, together with Meyer Steinberg from Brookhaven National Laboratory, has calculated the total HHV efficiencies for electric power generation through five different routes to the production of turbostratic carbons, including petroleum coke, refinery products, natural gas, and lignite coal. The findings were 80 percent for direct petroleum coke, 67 to 75 percent for natural gas (methane), 72 percent for heavy oil, and 68 percent for lignite.

Costs Keep Things Interesting

An important aspect of the research effort is estimating costs for electrical production and for cell components. Petroleum coke is by far the least expensive source of fuel (costing as little as 5 cent per kilogram) because it is the byproduct of the oil refining industry. In the carbon black industry, the pyrolysis step costs about 20 cents per kilogram of carbon produced and thus would contribute about 3 cents to the cost per kilowatt-hour of electricity generated using carbon-black fuel.

At this time, cost estimates are difficult to make. A final design for the

Comparing Fuel Cells

Fuel cells use hydrogen, simple hydrocarbons such as methane, or carbon to produce electricity electrochemically rather than by burning them as fuels. Electrochemical means of providing electricity are generally much more efficient than burning fossil fuels in power plants to drive boilers and dynamos. The theoretical efficiencies of hydrogen or methane fuel cells top out at 69 percent and 90 percent, respectively, compared to 40-percent efficiency for typical power plants. The carbon–oxygen reaction that drives a direct carbon conversion fuel cell is unique: theoretically, all the potential combustion heat can be converted to electric power.

Methane and hydrogen fuel cells have other disadvantages. For one, the fuels are continuously diluted by their own reaction products as they are consumed. The voltage drops to ever-lower values, and as a result, not all of the fuel can be consumed. For carbon, no such dilution occurs, and all of the incoming fuel can be used to make electricity at about the same rate and voltage. Hydrogen, methane, and carbon fuel cells have practical voltage efficiency, that is, they operate at 80 percent of the maximum cell voltage.

The total electrical efficiency of a fuel cell is the product of three factors: theoretical efficiency, the fraction of fuel used, and the voltage efficiency. Carbon has a high total efficiency because of the favorable thermodynamics of the carbon–oxygen reaction. The actual efficiencies of the hydrogen and methane cells achieved in pilot plants are listed in the table below.

Of course, different kinds and amounts of energy are used in making these fuels. Methane needs only to be extracted from natural gas—a low-cost technology. Hydrogen can be produced from nuclear and renewable energies without any production of carbon dioxide. Carbon can be derived at a low energy cost from nearly any fossil fuel.

Comparison of efficiencies of fuel cells

Fuel	Theoretical limit	Fraction of fuel used in practical operation	Fraction of voltage available at practical rate	Total efficiency (higher heating value)
Carbon	1.01	1.0	0.8	0.80
Hydrogen	0.69	0.75 to 0.85	0.8	0.41 to 0.47
Methane	0.90	0.75 to 0.85	0.8	0.54 to 0.61

(Operating temperature of 750°C. Energy cost of fuel synthesis is excluded.)

hardware has not been settled on, and increases in power density are expected that inversely affect hardware size and cost. Nevertheless, the cost of the most expensive part of the cell—the commercial ceramic matrix holding the electrolyte and electrodes—is about $200 per square meter (that is, about $200 per kilowatt at 1 kilowatt per square meter). By comparison, modern gas turbine plants generate power at about $350 per kilowatt. Currently, the cost of cell hardware is low enough to be interesting.

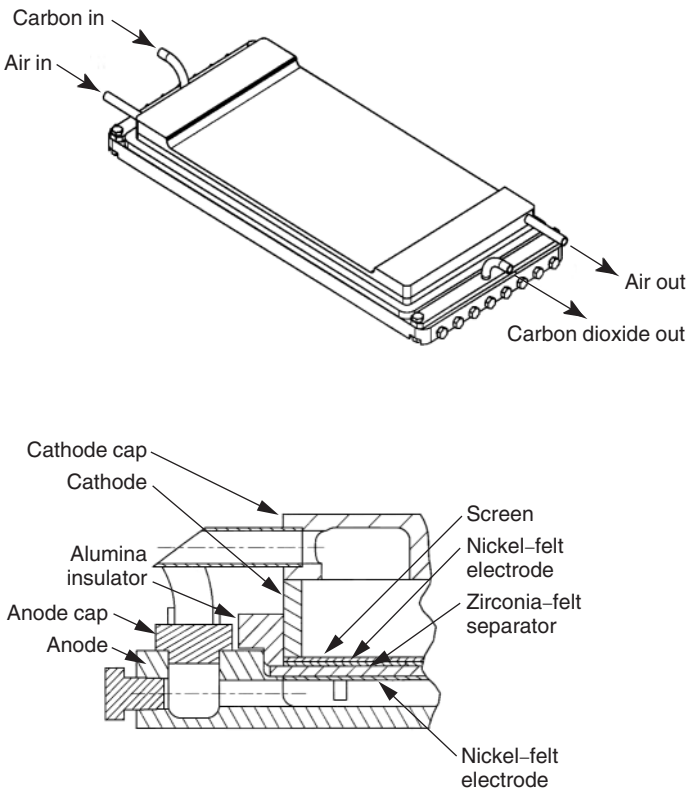
The sheer simplicity of the cell contributes to keeping costs down. The cell's fundamental thermodynamic properties mean almost no waste heat and full fuel consumption. Also, because the carbon conversion process produces pure carbon dioxide ready for sequestration or industrial use, cell design does not need costly components to collect and scrub the carbon dioxide before storage or use.

Finally, cell components and fuel are nontoxic and relatively hazard-free. In particular, because the carbon–molten salt slurry does not explode if inadvertently brought into contact with air, no explosion-prevention safeguards need to be engineered into the cells.

Destined for the Grid

Cooper is thinking ahead to the day when direct carbon conversion units could be used to generate electric power for the grid. Such a power plant would be "large, but not gigantic." A 3-gigawatt direct-carbon-conversion power plant, big enough to continuously supply some 3 million homes with about 1 kilowatt each, would only be the size of a large, two-story office building.

To achieve commercial adoption, however, requires greater understanding of the underlying science, especially the three-way relationship between conditions of pyrolysis, the resulting carbon nanostructure, and the electrochemical reactivity. While pyrolysis of natural gas and oil products to make turbostratic carbons is well known and widely practiced, the extraction of carbon from coal is less developed. "The extraction of carbon from coal, for example, by



An advanced cell design scales up the dimensions of tested cells to the 1,000-square-centimeter level. A maximum of 100 watts is expected from this design.

Nerine Cherepy and John Cooper assemble an experimental carbon conversion fuel cell.

Key Points to Understanding Carbon Conversion and Its Potential

- No single solution exists to meet 21st century energy and environmental needs. Electrification of highway vehicles, conservation, advanced turbines, electrochemical conversion of fuels (as with direct carbon conversion), nuclear power, and renewable energy are all likely to be important.
- It is critically important to develop technologies that generate electric power much closer to theoretical limits—the best large-scale commercial technologies are only halfway there.
- Direct carbon conversion generates electricity from reacting carbon and oxygen in a fuel cell and makes a pure carbon dioxide product available for industrial use or sequestration.
- Using fossil energy as carbon in a carbon fuel cell produces little waste heat and consumes all the fuel in a single pass, thereby bringing total efficiencies of 70 to 80 percent into reach.

hydropyrolysis, needs to be developed if this approach is to aid the conversion of 50 percent of Earth's fossil fuels," says Cooper.

The team is planning to scale up a demonstration unit from the 3-watt experimental cell to a stackable, 100-watt engineering module with 1,000 square centimeters of active area. The large-scale experiments should reveal any materials and operational problems on a practical scale, especially during extended tests.

Meanwhile, the team is testing more carbon blacks from commercial suppliers and turbostratic carbon fuels from new sources, such as petroleum cokes and coals. The tests with coal will be particularly important because of its large-scale reserves.

Cooper points to the complex task of providing energy while controlling greenhouse gases, particularly carbon dioxide. "The solution is beyond the scope of power production technology alone," he says, noting that electrical energy production currently accounts for just one-sixth of the total output of carbon dioxide. "Advanced combustion, fuel cells, nuclear and renewable energy, and conservation may all combine to help the situation in a way that cannot presently be predicted."

The Livermore team considers it vitally important to develop a simple fuel cell technology that greatly increases the yield of electric energy from each unit of fossil fuel, uses fuels derived efficiently from almost any fossil fuel, significantly decreases the carbon dioxide released into the atmosphere, and makes it easy to capture the carbon dioxide for sequestration or other use.

Clearly, we're just beginning to hear about direct carbon conversion.

—Arnie Heller

Key Words: biomass, carbon black, carbon dioxide, coal, direct carbon conversion, fuel cell, global warming, hydrogen fuel cell, hydropyrolysis, natural gas, petroleum coke, pyrolysis, turbostratic carbon.

For further information contact John Cooper (925) 423-6649 (cooper3@llnl.gov).

About the Scientist

JOHN COOPER received his B.A. in chemistry from Pomona College in 1968 and his Ph.D. in chemistry from the University of California at Berkeley in 1975. For 25 years, he has specialized in electrochemical science and engineering, with particular emphasis on fuel cells, fuel batteries, and power generation using reactive metals, zinc, aluminum, or elemental carbon with air-depolarized cathodes. He led the DOE National Program to develop novel metal–air fuel batteries for electric vehicle propulsion. He assembled and led a team to develop advanced processes for the growth and production of optical crystals for lasers. In addition, he has led projects to develop advanced processes, such as molten-salt oxidation, for treating mixed waste and military waste.

Currently, Cooper is scientific capability leader for electrochemistry and corrosion in the Chemistry and Materials Science Directorate. He is also the technical director of a private-sector collaboration to develop zinc–air fuel cells and batteries and is the inventor–director of projects to develop practical high-efficiency carbon–oxygen cells for mitigating the greenhouse gas emissions associated with electric power generation.

Environmental Research in California and Beyond

From earthquake prediction to groundwater quality, environmental research projects focused on California have implications far beyond the state's borders.

EARTH, air, fire, water . . . Aristotle's four basic elements of matter come under a great deal of scrutiny in many of the environmental and geologic projects at Lawrence Livermore. Some of this research springs from issues of particular interest to California, such as groundwater quality or earthquake prediction.

The Energy and Environment Directorate, with the help of other groups across the Laboratory, is a natural for contributing in this arena. For example, Robin Newmark, a geophysicist in Energy and Environment, helped develop thermal remediation technologies such as dynamic underground stripping and hydrous pyrolysis/oxidation that are being used to clean up contaminated groundwater sites at both government and privately owned facilities across the country. These technologies have been used at Lawrence Livermore and in Visalia, California, and are under consideration by the U.S. and California Environmental Protection agencies for use at other sites. She notes, "We have a number of small and mid-sized projects with a California perspective, and others that have great potential for more interplay with the state community."

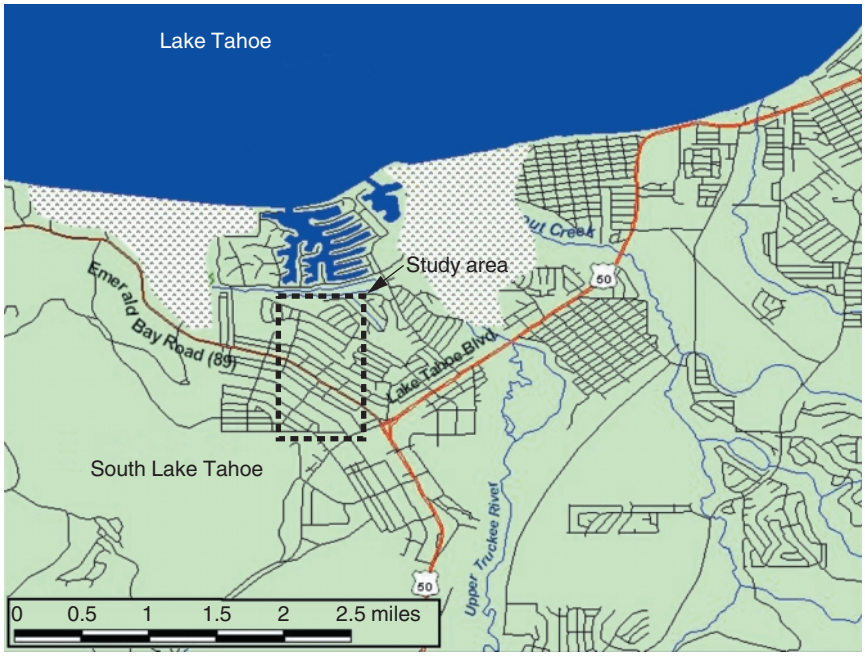
Dave Layton, division leader for Health and Ecological Assessment, agrees. "I'd like to see our research portfolio push further into California."

In one current project funded by the California State Water Quality Control Board, researchers from Energy and Environment, along with colleagues from the Chemistry and Materials Science Directorate and the Environmental Protection Department's Environmental Restoration Division, are using isotopic tracers to examine the vulnerability of groundwater to volatile organic compounds and other chemicals. Meanwhile, out on dry land, researchers from the Biology and Biotechnology Research Program and

the Energy and Environment directorates are developing a DNA-based measurement technology that will help them study the environmental factors that allow the Valley Fever fungus to thrive in California's Central Valley. Another California-centric example is a recent workshop hosted by the Laboratory and sponsored by the Department of Energy's Office of Fuels Development and the Western States Petroleum Association. The workshop focused on the increased use of ethanol and alkylates in automotive fuels in California after a phaseout of the potentially toxic MTBE fuel additive.

Unique Laboratory capabilities are also being used to help California with environmental issues. The Atmospheric Release and Advisory Capability (ARAC) came to the aid of the California Environmental Protection Agency three years ago, using computer simulations to monitor smoke billowing from a 30-acre tire fire near Tracy, California (see *S&TR*, June 1999, pp. 4–11). The Environmental Restoration Division developed GeoTracker, a public Web site (http://geotracker2.arsenaultlegg.com/), which helps California regulators and the public evaluate the safety of drinking water by identifying leaking underground fuel tanks and their proximity to municipal water wells (see *S&TR*, July/August 2000, p. 2). A digital mapping or geographic information systems capability that allows users to sift through layers of geographic data (such as population densities, elevation data, and earthquake faults) will support the California Energy Commission in siting future power plants to alleviate the current California energy crisis.

Three projects with a subterranean focus—two on groundwater and one on earthquakes—provide examples of what the Laboratory is doing to address environmental issues of importance to California and beyond. In a fourth, large-scale effort—a joint vision of Lawrence Livermore and the University of California at Merced—environmental research related to the California Central Valley and the Sierra Nevada would be integrated into a supercomputer- and sensor-driven "Virtual Valley," with resources available to planners and public alike.



Map of a portion of South Lake Tahoe showing the area being modeled to determine how MTBE moves in groundwater.

Assessing MTBE Mitigation

Since 1992, many U.S. oil refineries have been adding MTBE (methyl tertiary-butyl ether) to gasoline to reduce air pollution and fulfill a requirement of the federal Clean Air Act. However, MTBE has turned out to have certain drawbacks. Once it gets into the ground—through spills and leaks—it can infiltrate groundwater supplies, giving drinking water an unpleasant taste and odor. "The taste is noticeable even at very small quantities—down to 5 micrograms of MTBE per liter of water," notes Laboratory hydrogeologist Steven Carle. Some evidence also suggests that MTBE may be a human carcinogen.

These are no small issues. Groundwater is a significant source of drinking water worldwide. In the United States alone, 60 percent of the water used is groundwater. In California, at least 10 public drinking water wells have been closed because of the intrusion of MTBE.

With this as background, Laboratory researchers Carle, Reed Maxwell, and Dave Layton developed three-dimensional computer simulations of how MTBE moves underground. As it turns out, MTBE behaves differently in groundwater from other petroleum products such as benzene: it is highly soluble in water, does not easily adsorb to soil, and does not degrade readily on its own. The team chose South Lake Tahoe as the location to model. "MTBE could be a crucial issue for this area," Carle says. "The South Lake Tahoe area receives lots of recharge in the spring from melting snow. The snow

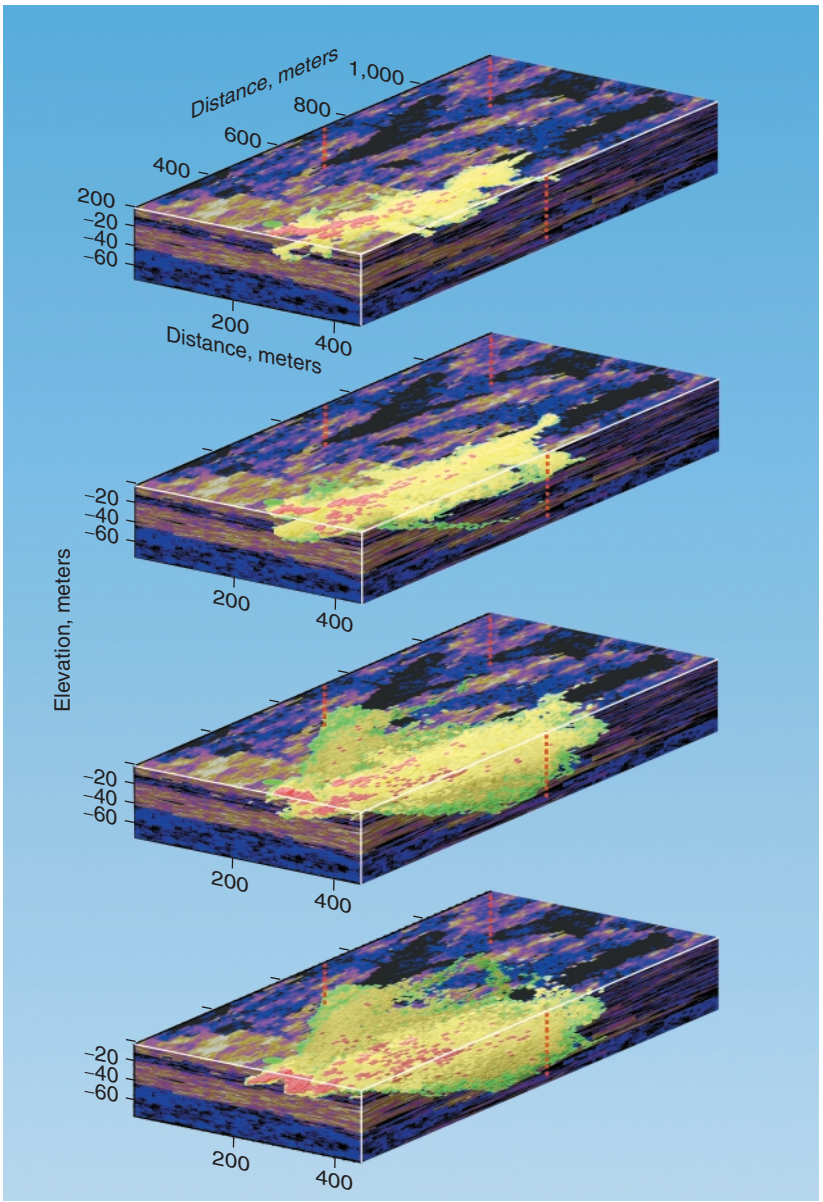
melts into the ground, causing pressure to build up that flushes the groundwater and anything in it quickly through the subsurface system."

Carle and the team set about creating a realistic geologic model of the area using information supplied by the South Lake Tahoe Public Utilities District. The subsurface is complex, notes Carle, with the aquifer systems spanning multiple geologic formations. Using TSIM, a geostatistical simulation code developed by Carle, the researchers built a below-surface model of the geology of the area as well as of the permeability of the various layers and subterranean features.

"We had to use a certain amount of statistical interpolation," says Carle. "Even though we used information gained from core samples and geologic studies of the area, we don't know, inch by inch, exactly what's down there." The model of the area—a chunk of real estate 600 meters by 1,200 meters—was built up of 7.2 million wafer-thin geologic "cells," 5 by 10 by 0.2 meters. "We ended up with a problem consisting of millions of cells, with materials that had permeabilities differing by seven orders of magnitude," he says. It was the first time that both the geology and permeability of this area had been simulated in such detail.

The team then placed four municipal wells in the model at their proper locations and set up a realistic model of a leaking underground tank: a constantly replenished pool of MTBE (1.5 kilograms per day) just under the surface, dissolving into groundwater over 300 days. Knowing the pumping rates of the wells, the team was able to use ParFlow (a parallel finite-difference numerical flow modeling code developed at the Laboratory) to calculate a high-resolution flow field. The flow field indicates the direction that water and other liquids flow below the surface, rather like a topographic map allows determination of the direction of flow on the surface.

Finally, the simulations were fed into SLIM-Fast, a numerical particle-tracking code, to trace the fate of MTBE. "With this code, tracking MTBE particles in the groundwater is like tracking a bunch of ping-pong balls in a river," explains Carle. SLIM-Fast also permits "splitting" of the MTBE particles, allowing researchers to track increasingly dilute concentrations of MTBE. "This was a first," notes Carle. "Most other codes cannot trace the ultimate fate of MTBE because they can't accurately reach the low concentrations that evolve over time." Using the three codes, the researchers tracked the MTBE over a 30-year period to its final dilutions in the wells.



This four-part simulation shows an extensive MTBE plume increasing the contamination of nearby wells over time.

The team also generated multiple scenarios using different geologic heterogeneities, all equally based on the information available, all equally plausible. "We generated a 'cloud of predictions' that helped us determine the uncertainties of our final results," says Carle. The bottom line: According to the simulations, the most likely path of flow for MTBE leads directly to the water wells where it would show up in concentrations of tens of micrograms per liter.

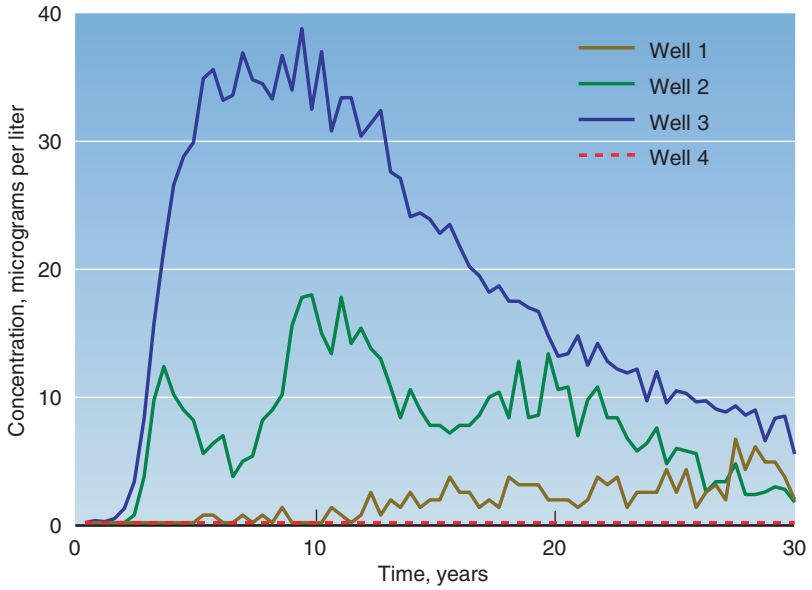
When the results were compared to an actual situation, the researchers found they were definitely in the ballpark. MTBE was found in seven South Lake Tahoe wells in concentrations of 0.5 to 68 micrograms per liter. One interesting result of the simulations indicates that the MTBE problem could persist for decades. "This was something we hadn't expected," says Carle. "We'd assumed—as did others in the field—that the MTBE moves along at the pace of groundwater. Instead, it appears that, through mechanisms we don't fully understand yet, the MTBE lingers and is released over time. It could be that the chemical is slowing down in low-permeability zones. To explore this issue and others requires more realistic simulations that can produce better predictions."

A (Water) Bug's Life

Chemicals aren't the only undesirables in the groundwater supplies. Microbes, viruses—"bugs" in popular parlance—also find a welcome environment in subterranean aquifers. Livermore's Reed Maxwell worked with fellow researchers from the Laboratory, the U.S. Geological Survey, and Drexel University to better understand how these organisms are transported underground. Specifically, the team applied simulation and modeling techniques to see how the varied geology of riverbanks—sand, clay, cobbles, gravel, and so on—affect the movement of colloids (submicroscopic particles, such as viruses) dispersed in a different medium, such as water. Using a site in California's Orange County for their simulations, the researchers examined how viruses could attach to different geologic media and compared the arrival time at the wells for both viruses and tracer chemicals often used to track groundwater movement. They also compared their results with results of simulations using models that assume a uniform, or homogeneous, type of material throughout—a riverbank composed of only sand, for instance.

"Water management districts such as Orange County are looking for better ways to manage and obtain clean sources of drinking water," notes Maxwell. "In the process, researchers are examining technologies used over the past century in other countries and finding that these methods are actually quite effective in producing clean water." For instance, a number of European countries obtain their water from the Rhine River by placing a well on the riverbank and pulling in river water through the subsurface of the bank. This riverbank filtration technique filters out much of the microbial activity in the water. "We'd like to better understand how this process works," says Maxwell. "At what rate are these organisms filtered out? Do they stick to some particular medium, and if so, what medium and for how long? How does the transport of these colloids differ from that of tracer chemicals?"

These questions are of particular interest to Orange County. Nearly 80 percent of its water supply is composed of groundwater. The Orange County Water District is currently monitoring surface water and groundwater for viruses, but so far, it has detected none. Furthermore, Orange



Simulated MTBE breakthrough curves, showing concentration of MTBE in wells over time out to 30 years.

County is now considering using tertiary-treated wastewater (wastewater treated three times) to artificially recharge lakes, which will, over time, recharge groundwater aquifers. The Environmental Protection Agency has guidelines in place to ensure that such water is clean before it's used again.

Maxwell explains, "There are guidelines on such matters as the distances that wells must be from the water sources, and the 'residence time' that treated water must remain underground. These guidelines are expected to account for complicated natural processes that need to be better understood. Both wastewater recharge and riverbank filtration are potential pathways for microbes to contaminate drinking water sources, so understanding how various geologic media affect movement of these organisms is important."

To gain insight into how viruses move in groundwater and potentially prevent virus problems before they arise, Maxwell and his collaborators used a three-dimensional computer model developed by Laboratory hydrologist Andrew Tompson to simulate the movement of groundwater in an area used in a water reclamation operation managed by the Orange County Water District.

Three wells were studied. Two (PL--5 and PL-10) derive much of their water directly from the Santa Ana River, and one (P-4) receives recharge water from Anaheim Lake and Warner Basin, which in turn receive their water from the river. Water arriving at P-4 was about 1.3 years old, water at PL-5 was 0.5 year old, PL-10 water was 1.2 years old. Although PL-3 is closer to the water source than PL-5, the same water actually takes longer to travel the shorter distance because of the permeability and complexity of the subsurface. This anomaly, Maxwell notes, would not have appeared if the geologic model had been homogeneous.

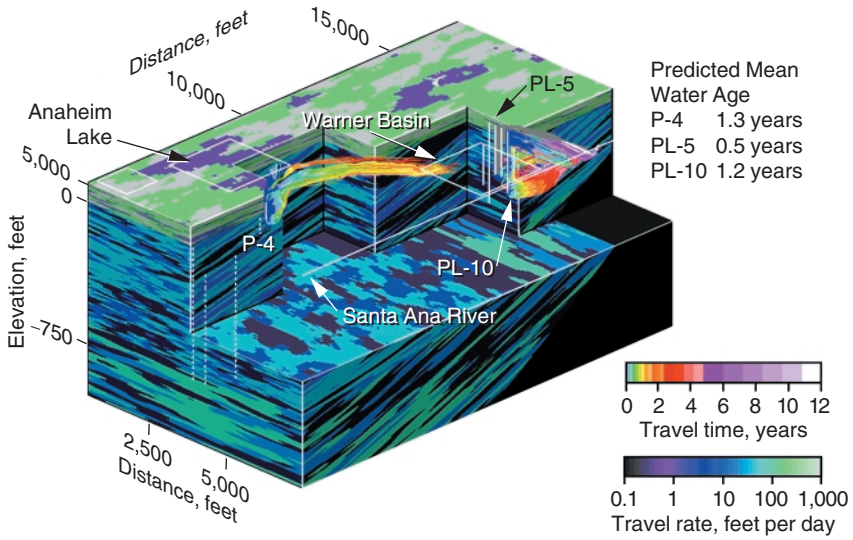
The team took this three-dimensional model and numerically built in the ways in which submicrometer-size organisms attach and detach from the materials found beneath the surface. From there, the team deconvolved the problem. That is, they took the complicated three-dimensional flow field that simulates the motion of groundwater, its tracers, and its hitchhiking organisms and broke it down into a number of one-dimensional transport problems. The problems were solved using Livermore's massively parallel computing systems. The results were then recombined to find out what arrived first at the wells.

A tracer chemical was first to break through into the simulated wells and displayed the highest concentrations at the wells over time. The viruses broke through last and showed the lowest concentrations. "What that told us is that the well is most vulnerable to a tracer . . . not to microbes." says Maxwell. "Tracer chemicals, in other words, are poor predictors of viral arrival times in wells according to this particular model. These results show the importance of using a model that accurately reproduces the geology of the given area."

There are, he adds, many more questions regarding microbial transport in groundwater. "It's pretty clear that different filtration processes dominate for different types of soil. Less permeable sediments—tightly packed sand, for instance—are good at filtering out microbes. We still have a ways to go in understanding the physics of viral transport in the subsurface."

In Search of Ancient Earthquakes

What could be more California than earthquakes? The San Francisco Bay Area has the highest density of active faults and the highest rate of seismic moment release per square kilometer of any urban area in the U.S. In 1998, in the hope of providing a framework for more precise forecasts of future large and damaging quakes, the Center for Accelerator Mass Spectrometry (CAMS) at Livermore joined a multi-institutional effort, led by the U.S. Geological Survey, in a region-



Computer simulation of the subsurface geology, the streamlines tracing travel paths of groundwater, and the predicted mean age of the water as it travels from recharge sources to wells P-4, PL-5, and PL-10.

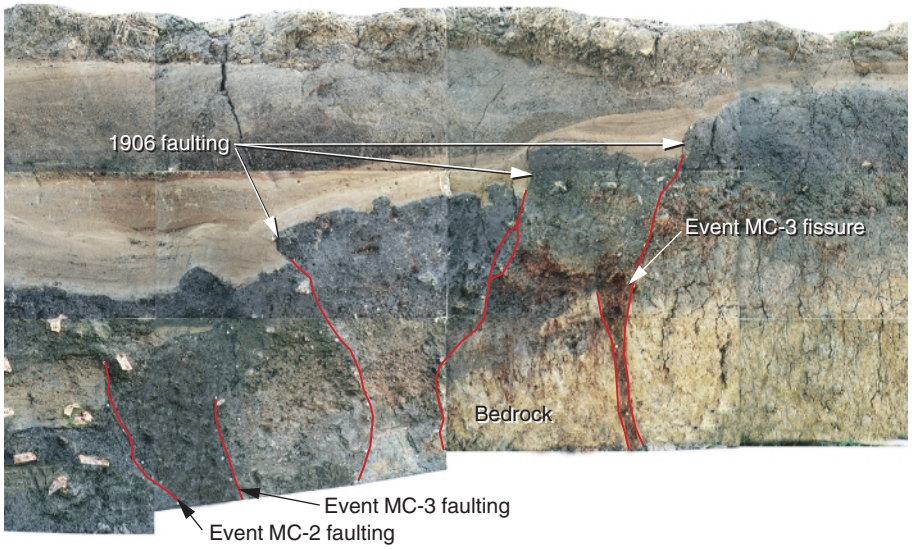
wide cooperative project called the Bay Area Paleoseismic Experiment, or BAPEX.

BAPEX's goal is to develop a 2,000-year chronology of large earthquakes in the Bay Area and look for patterns in the timing, locations, and magnitudes of prehistoric shakers. Unlike other paleoearthquake projects, which usually limit their focus to the history of a single fault, BAPEX targets essentially an entire plate boundary. This region—the 45-kilometer-wide area between the San Gregorio and Greenville fault zones from west to east—represents most of the plate boundary between the Pacific and North American plates. As part of that effort, geologists such as Livermore's Gordon Seitz are focusing on the area's seven major fault systems—the San Andreas, San Gregorio, Hayward, Rodgers Creek, Calaveras, Concord–Green Valley, and Greenville.

Seitz explains, "When we find a promising site, we excavate down as far as 9 meters and examine the geologic layers or strata. Although most earthquakes are triggered 10 to 15 kilometers below the surface, large earthquakes cause ground rupture,

The San Francisco Bay Area is located within the Pacific–North American plate boundary. The focus of the Bay Area Paleoseismic Experiment has been to develop past earthquake chronologies on the seven major faults in the area: the San Gregorio, San Andreas, Hayward, Calaveras, Rodgers Creek, Concord–Green Valley, and Greenville faults.

This photomosaic trench log, a vertical cross section of the San Andreas Fault at Mill Canyon near Watsonville, California, shows evidence of three past earthquakes—the San Francisco earthquake of 1906 and two previous events labeled MC-2 and MC-3. Each of these earthquakes produced characteristic downward-tapered infilled fissures. (This study was led by Tom Fumal at the U.S. Geological Survey.)

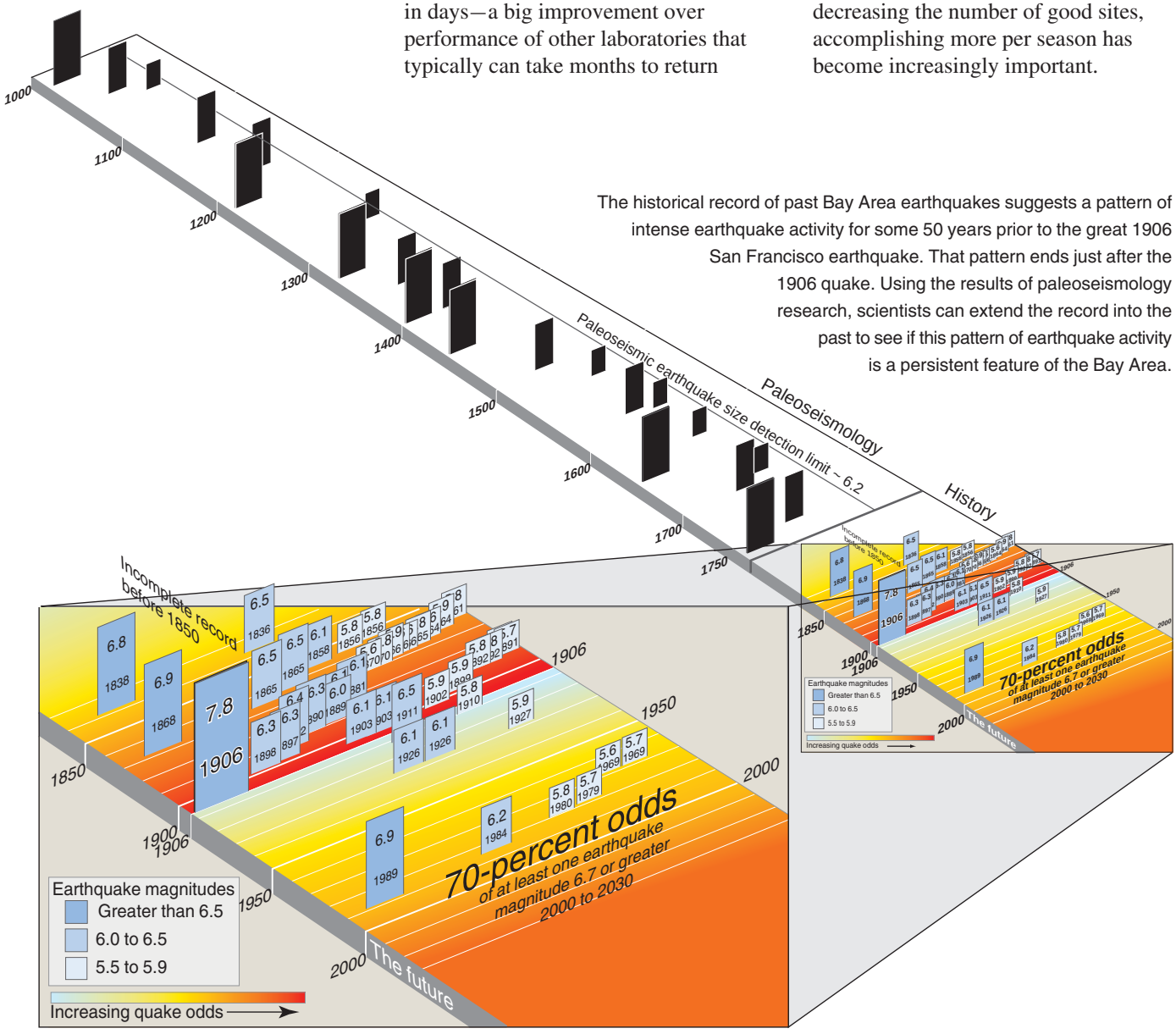


Lawrence Livermore National Laboratory

which is recorded in these near-surface layers." In cross-cuts through the strata of a fault zone tens of meters in width, the researchers look for evidence of former ground-rupturing deformation such as fault scarps at the surface or buried beneath it, fissure fills, upward-terminating faults, folds, and sand volcanoes. When geologists find such layers, they look for organic material within the sediments that can be carbon dated at CAMS.

Not much material is required for dating. About one-thousandth of a gram—an amount equal to a couple grains of dirt—will do. The age of the material is determined by the amount of carbon-14, or radioactive carbon, in the sample. The Livermore accelerator is extremely sensitive, able to find one carbon-14 isotope among a quadrillion other carbon atoms. (For more information on CAMS, see *S&TR*, July/August 2000, pp. 12–19.)

The CAMS team can produce results in days—a big improvement over performance of other laboratories that typically can take months to return results to field geologists. "We call it real-time dating," says Seitz. With CAMS as part of the process, geologists can quickly determine the age of key layers and move on to the next step in their fieldwork. "What used to take several seasons can now be accomplished in one season," he adds. This quick turnaround is particularly important when the cross-cut or trench is located in an urban area and cannot be left open for more than a few days. And with urban development decreasing the number of good sites, accomplishing more per season has become increasingly important.



The historical record of past Bay Area earthquakes suggests a pattern of intense earthquake activity for some 50 years prior to the great 1906 San Francisco earthquake. That pattern ends just after the 1906 quake. Using the results of paleoseismology research, scientists can extend the record into the past to see if this pattern of earthquake activity is a persistent feature of the Bay Area.

BAPEX geologists have excavated more than 28 Bay Area paleoseismic sites and determined over 900 radiocarbon dates at CAMS. In the process, they've developed earthquake histories covering several thousand years for individual faults. To do a rigorous statistical analysis on the earthquake patterns, Seitz estimates that they need more event records covering longer periods of time. "Fourteen is the most I've seen recorded on any one site," he notes.

When a comparison of timing and magnitudes is made between "historic" northern California earthquakes (1850 to present) and "prehistoric" quakes, a pattern emerges: Leading up to the 1906 quake, the magnitude and frequency of earthquakes increased; after 1906, activity shut off for more than 50 years. Is the Bay Area at the start of another cycle, with the1989 Loma Prieta quake being the first major quake?

"We can't say for certain," says Seitz. "Historically, the Bay Area has not experienced one complete earthquake cycle. But by the best estimate of the experts, there's a 70-percent chance in the next 30 years that the Bay Area will see a quake of magnitude 6.7 or greater quite possibly centered in a heavily populated urban area. BAPEX should cast some additional light on these forecasts by providing a more complete picture of earthquake patterns over time and space."

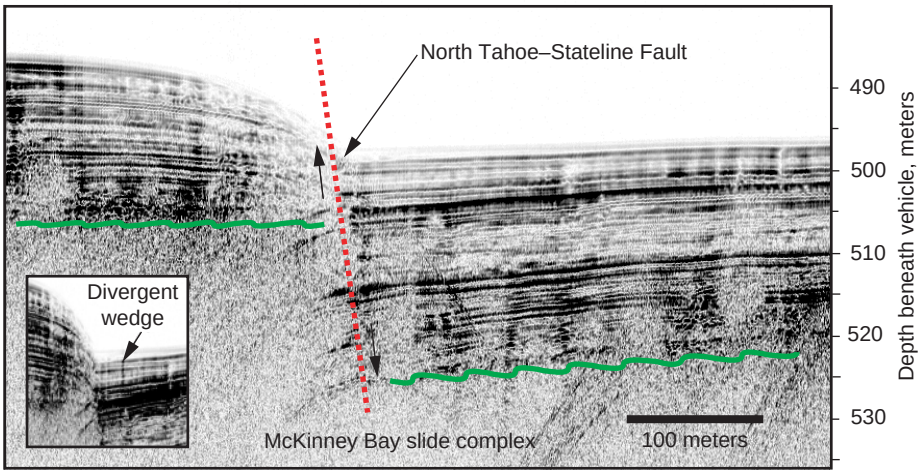
Seitz, along with Graham Kent of the Scripps Institution of Oceanography at the University of California at San Diego, is extending this research by taking a close look at paleoearthquakes under water. "Previously, the research of paleoearthquakes has focused on dry land," he explains, "because underwater trenching is not yet possible. But in light of several major technological advances—high-resolution seismic imaging, accelerator mass spectrometry's ability to provide carbon-14 analysis of small samples, and detailed bathymetry mapping—we wondered how fault investigations could be done offshore."

Seitz and Kent turned to a new high-resolution seismic technique called CHIRP to help with underwater paleoseismic studies. Like a sonar system, CHIRP bounces sound waves off submerged structures. However, unlike sonar, the CHIRP system can image sediment layers beneath the lakebed at unprecedented resolutions. "With CHIRP, we can image layers as thin as 20 centimeters," he says. Using Lake Tahoe as a test bed, the team created seismic profiles at the bottom of the lake with imaging depths of as much as 50 meters.

The use of CHIRP technology in seismic hazard assessment is new, notes Seitz. Skills learned at Lake Tahoe will not only help solve many of the outstanding local questions, but in the future, they could also be used to understand a subset of neotectonic problems that are hidden underwater.

Says Seitz, "Our approach of 'acoustic trenching' combined with carbon dating of strategically located sediment cores will, we hope, allow future studies of many active fault systems that have been largely ignored, mostly because of water coverage. Being able to image the tectonically deformed sediments under water and having a way to determine their age are key."

Offshore faults along the California coastline and the parts of faults that extend offshore are examples of largely ignored fault systems that would benefit from underwater peleoearthquake research. International locales such as the Marmara Sea adjacent to quake-threatened Istanbul would also benefit from this technological advance. For Seitz, "Lake Tahoe is an ideal place to develop these techniques. The



A seismic profile at unprecedented submeter resolution across the North Tahoe–Stateline Fault at a water depth of about 500 meters. The unique high resolution of this profile is achieved by sweeping the source through a range of frequencies (500 hertz to 15 kilohertz), a technique developed largely by Neal Driscoll, now at the Scripps Institution in San Diego. The thickening of sediments near the fault on the downthrown right side block is characteristic of sedimentation after an earthquake.

logistics are easier on this lake than at sea, and ship costs are 5 to 10 times less expensive."

Entering the Virtual Valley

Suppose one could take the Laboratory's environmental research capabilities and projects, join them to the research capabilities of a leading university, and focus them on a particular region. This is the premise of the Virtual Valley, a joint vision of Lawrence Livermore and the University of California at Merced, UC's newest campus, which is in the planning and development stage.

The Laboratory's activities to implement such a Virtual Valley concept would be pursued in partnership with those of UC Merced's Sierra Nevada Research Institute. The institute has been chartered to focus on the challenges surrounding the rapid development and transformation of California's Central Valley and Sierra Nevada region.

The task facing Virtual Valley designers and planners is to provide a comprehensive environmental simulation and observation system focused on regional issues. Issues the Virtual Valley might tackle include wildfire management and prediction, the effects of urban development, air quality and water resources management, earthquake prediction, and groundwater management and cleanup. The Virtual Valley will have the information, tools, and computational power needed to explore all these topics and more.

The Virtual Valley would tie together supercomputers, sensor networks, geographic information systems, field measurement sites, historical data sets, wireless communications simulation and modeling, advanced visualization systems, and Internet access. Its data sets and computing power would be available to students, educators, scientists, planners, residents, and the public-at-large.

Users would be able to combine diverse areas of environmental research together, look for commonalties, determine causes and effects, and work from a common platform. The effects of this research have the potential of reaching beyond California's borders. For example, other areas in the United States have groundwater management issues. Other countries must deal with the specter of devastating earthquakes. The Virtual Valley—and all of the research that could feed into it—provides us with a way to benefit the world, by focusing on the valleys and mountains out our backdoor.

—Ann Parker

Key Words: Bay Areas Paleoseismic Experiment (BAPEX), Center for Mass Accelerator Spectrometry (CAMS), CHIRP, groundwater management, hydrogeology, MTBE, Orange County, paleoearthquakes, ParFlow, San Andreas Fault, SLIM-Fast, South Lake Tahoe, TSIM, University of California at Merced, Virtual Valley.

For further information contact Steve Carle (925) 423-5039 (carle1@llnl.gov), Reed Maxwell (925) 422-7436 (maxwell5@llnl.gov), or Gordon Seitz (925) 423-8469 (seitz3@llnl.gov).

About the Scientists

REED MAXWELL (left) holds a B.S. from the University of Miami (1992) and an M.S. from the University of California at Los Angeles (1994) in mechanical engineering, and a Ph.D. from the University of California at Berkeley (1998) in civil and environmental engineering. He joined the Laboratory as a postdoctoral fellow in 1998 and became a physicist in the Geosciences and Environmental Technologies Division in 2000. He specializes in the study of radionuclide transport at the Nevada Test Site and in environmental risk assessment and management.

STEVE CARLE (center) received his B.S. and M.S. in engineering geoscience from the University of California at Berkeley in 1986 and 1987, respectively, and his Ph.D. in hydrologic science from the University of California at Davis in 1996. He came to Livermore as a postdoctoral fellow in 1997. In 2000, he joined the Geosciences and Environmental Technologies Division as a physicist. His research focuses on the development of geostatistical methods, the hydrogeologic modeling of groundwater flow and contaminant transport, and the integration of diverse data sets.

GORDON SEITZ (right) holds a B.S. in geology from San Diego State University (1983) and a Ph.D. in geological sciences from the University of Oregon at Eugene (1999). He joined the Laboratory as a postdoctoral fellow in 1999 to work at the Center for Accelerator Mass Spectrometry on the Bay Area Paleoseismic Experiment. His research interests include improving scientific understanding of past earthquake chronologies and interpreting patterns of fault behavior in space and time based on accelerator mass spectrometry carbon-14 dating, with special emphasis on the San Andreas Fault.

This Nitrogen Molecule Really Packs Heat

NITROGEN is a critical ingredient in most explosives—think of TNT (trinitrotoluene), the ammonium nitrate used in the Oklahoma City bombing, and the Department of Energy's most sophisticated high explosive in nuclear weapons, TATB (1,3,5-triamino-2,4,6-trinitrobenzene).

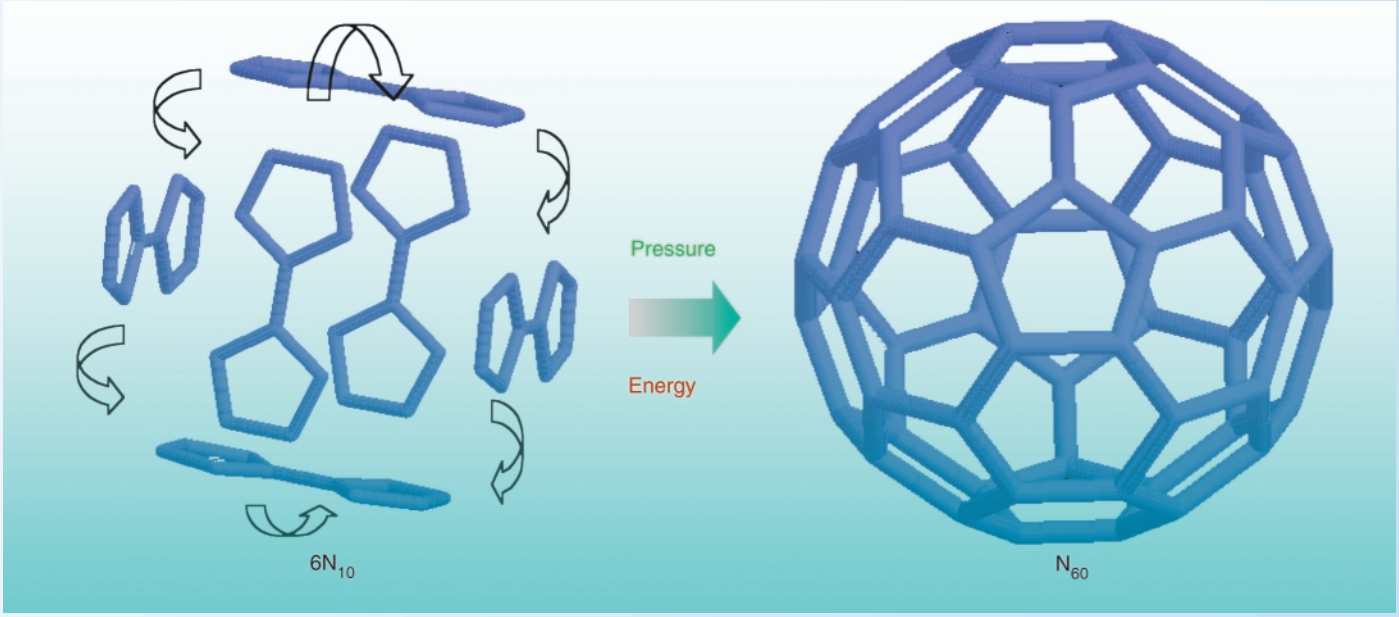
Huge amounts of energy are released when the tight bonds of a typical metastable (readily changed) energetic molecule are broken and the molecule reforms into smaller ones. A molecule composed solely of nitrogen atoms will release even more. For example, the tiny nitrogen anion N_3^- is a propellant used in automobile air bags. Because of the nature of nitrogen bonding, the explosive power of a molecule 20 times larger than N_3^- would be stunning.

Theoretical chemist Riad Manaa of Livermore may have found this unusual nitrogen molecule. His computer simulations show that it might be possible to join six 10-atom nitrogen molecules into a soccer-ball-shaped molecule known as a buckminsterfullerene—fullerene, for short.

Currently, the only fullerenes are large carbon molecules, with from 32 to as many as 600 atoms. A nitrogen fullerene would truly be an oddity, because the only forms of nitrogen known outside the laboratory are N_2, the most abundant element in our atmosphere, and the highly explosive N_3^-. In the laboratory, other forms of N_3^- as well as N_4^+ and N_5^+ have been created successfully. However, of these, all but N_5^+ were short lived.

The first fullerene, a 60-atom carbon molecule, was created in the laboratory in 1985, winning its discoverers a Nobel Prize in 1996. Says Manaa, "With their remarkable, perfect symmetry, fullerenes continue to create enormous excitement among scientists." Fullerenes are named for R. Buckminster Fuller, whose popular geodesic dome is structurally similar to a fullerene molecule. Also known as buckyballs, the closed, hollow carbon fullerenes have been produced in bulk quantities in the laboratory and show promise for use as superconductors and molecular containers. Their cage shape also makes them excellent building blocks for carbon-based nanotechnology.

With their high energy density, large nitrogen molecules would be prime candidates for new high explosives or perhaps for a novel propellant. Supersonic transport vehicles, for example, must achieve extremely high speeds. A new propellant that incorporated nitrogen fullerenes could generate the high thrust (energy release) needed to attain those speeds.



A combination of six molecular units of N_{10} form the nitrogen fullerene, N_{60}.

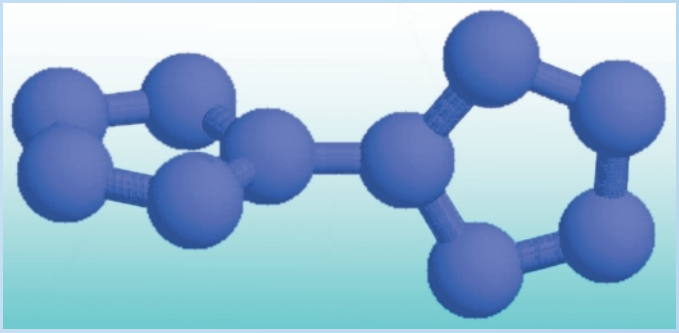
The Search Is On

Both the U.S. Air Force and the Department of Defense's Defense Advanced Research Projects Administration (DARPA) have funded research at Livermore and elsewhere to find a way to destabilize the strong N_2 triple bond, the second strongest covalent bond in all of nature. The goal is to find polymeric forms of nitrogen with single and double bonds, which are significantly weaker. Experiments with a diamond-anvil cell that pressurized N_2 up to almost 200 gigapascals failed to find a polymeric form of nitrogen. Shock compression experiments at high temperatures and pressures were equally unsuccessful. Only by direct synthesis in the laboratory have scientists been able to create any new polynitrogen phases.

Thus far, the N_3^-, N_3^+, and N_4^+ molecules created in the laboratory had a linear structure and were unstable because of their weak bonding. Only the N_5^+ molecule demonstrated long-term stability. Extensive research continues, however, on such exotic species as a tetrahedral N_4 and a cubic N_8. To date, quantum-chemistry-based computational studies predict that they will be at least metastable.

Because nitrogen atoms so clearly like to be triple bonded, no one had previously examined the possibility of creating a nitrogen fullerene. Manaa was thus the first to suggest that a super-high-energy molecule N_{60} was a possibility. He has shown that N_{60} could be formed from six units of bicyclic N_{10} molecules, which are themselves formed from two units of N_5. Using several quantum-chemical methods, he determined the structure and spectroscopy of the N_{10} molecule.

Simulations based on first-principles quantum chemistry accurately predict the chemical properties of atoms and molecules. The technique uses quantum mechanics to determine the distribution of electrons around each atom. From this electron distribution, any chemical property can be determined, including the structures and energies of the molecules.



The two pentazole ions (N_5^+ and N_5^-) that constitute dipentazole (N_{10}) are flat and connected perpendicularly to one another.

Such simulations showed that N_{10}, or dipentazole, would contain a mixture of single and double bonds and would be metastable. Each of its two pentazole ions (N_5^+ and N_5^-) would be flat, long lived, and connected perpendicularly to one another. The bridging bond between the ions appears to be strong and yet flexible enough to allow movement between them.

Bringing six such molecules together into a 60-atom buckyball would be tricky. Says Manaa, "It would likely have to be prepared under extreme conditions, such as high pressure."

The resulting molecule would be purely single bonded. Breaking those bonds—splitting N_{60} into 30 triple-bonded N_2 molecules—would release 50 percent more energy than can be released by CL-20, the best performing explosive currently known.

Manaa now has several studies under way to examine the possibility of creating N_{60} and the stability of the resulting molecule. He has also begun to look at a possible boron fullerene.

This work is part of research on the properties of energetic materials for the Department of Energy's Stockpile Stewardship Program, which uses the supercomputing capabilities of the Accelerated Strategic Computing Initiative (ASCI). Manaa notes that the use of extensive and rigorous computational tools coupled with the relatively large size of these molecules renders the use of massively parallel platforms—such as ASCI Blue—of paramount necessity.

Still a Long and Winding Road Ahead

Manaa's simulated nitrogen fullerene and other polynitrogen molecules currently under study are still a long way from practical use. To create a propellant for supersonic transport vehicles, the material being considered must first have a high energy density. It must also be reactive and must release large amounts of energy while increasing the number of particles—for example, one N_4 molecule reacting and releasing two N_2 molecules. The reaction must be controllable, and the material must be easily synthesized.

Polynitrogens are certainly high-energy-density materials and highly reactive. Of the new ones under study, only N_5 shows stability. N_{60} still exists only in ASCI simulations. So Manaa is quick to note that these new forms of nitrogen are "still strictly hypothetical."

—Katie Walter

Key Words: Accelerated Strategic Computing Initiative (ASCI), fullerenes, high-energy-density materials, nitrogen.

For further information contact Riad Manaa (925) 423-8668 (manaa1@llnl.gov).

PEREGRINE Goes to Work

WHO knew decades ago that the storehouse of data on nuclear science and radiation transport that Lawrence Livermore was developing would one day be applied to cancer treatment? In the early 1990s, Livermore researchers began combining that huge database with Monte Carlo statistical techniques to create PEREGRINE, a new tool for analyzing and planning radiation treatment for tumors. Approved for use by the U.S. Food and Drug Administration last September, PEREGRINE—named for the patron saint of cancer patients—is beginning to find its way into hospitals and clinics.

In July 1999, Livermore licensed the PEREGRINE technology to the NOMOS Corporation of Sewickley, Pennsylvania, to commercialize it. NOMOS has been developing advanced radiation therapy solutions in the fight against cancer since the early 1990s and is a leader in the new field of inverse planning for radiation treatment. "NOMOS is very innovative," according to physicist Rosemary Walling, program manager for PEREGRINE at Livermore.

PEREGRINE is equally innovative. While several dose calculation systems dot the radiation planning landscape, PEREGRINE is the first to exploit the mathematical power of Monte Carlo statistics (see *S&TR*, October 1999, pp. 14–15, and May 1997, pp. 4–11). It took the computing revolution of the 1980s and 1990s to make Monte Carlo fast enough for use by clinicians.

When patients receive radiation therapy, they are bombarded by billions to trillions of particles. PEREGRINE Monte Carlo radiation transport algorithms determine the dose deposited in the patient by following the path of representative particles as they travel through the body. The probabilistic laws of modern physics prevent scientists from knowing the exact fate of each particle, but they do allow scientists to predict a distribution of how these particles, and their daughter products, interact in matter. By sampling millions of the trillions of particles that enter the body and recording the energy deposited by each as it travels through the body, PEREGRINE's Monte Carlo statistical method develops an accurate representation of the dose distribution.

The Livermore team and NOMOS worked together to prepare all necessary documents for FDA approval. NOMOS submitted the application to the FDA in October 1999 and got the good news not quite a year later.

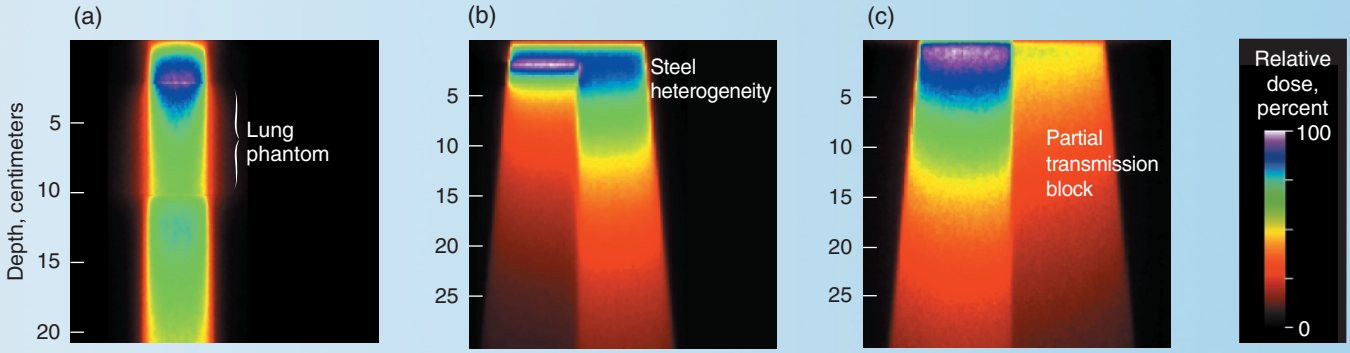
Former Secretary of Energy Bill Richardson announced FDA approval at NOMOS headquarters on October 6, 2000. "PEREGRINE could change the way cancer is treated in America," he said. "This technology was developed through advances resulting from nuclear weapons research and with the multidisciplinary scientific expertise of a Department of Energy national laboratory. This is an excellent example of turning swords into plowshares."

The FDA Decides

One of the biggest pieces of documentation that went to the FDA was a set of clinical measurements prepared in conjunction with cancer researchers at the University of California at San Francisco (UCSF). These measurements were important for verifying PEREGRINE's accuracy as a treatment tool. In radiation therapy, the goal is to maximize the radiation dose that hits the tumor while minimizing the dose to surrounding, healthy tissue. No clinical trials were performed for FDA approval. Rather, clinicians at UCSF used their accelerators (which create the radiation beam) to take measurements in water "phantoms" using various beam directions and angles as well as the many types of modifiers that are used to change the shape of the beam to match the needs of a particular tumor.

UCSF also took measurements with layers of various materials above and in the water phantom. PEREGRINE is unique in being the only dose calculation code that can examine radiation activity where different kinds of materials, such as bone, soft tissue, and air (in our lungs), meet. NOMOS staff took measurements in solid phantoms to duplicate bone and other materials.

Christine Hartmann-Siantar, program leader for the PEREGRINE project at Livermore, is shown with John Friede, chairman and chief executive officer of NOMOS Corporation during the announcement of FDA approval for PEREGRINE.



Images resulting from some of the PEREGRINE measurements taken by the staff at the University of California at San Francisco. They demonstrate how effectively PEREGRINE can handle different materials and shapes: (a) heterogeneities in the lung, (b) a steel prosthesis, and (c) a partial transmission block to protect healthy tissue during radiation treatment.

The NOMOS submission to FDA requested what is known as 510(k) approval. A 510(k) is a premarketing notification demonstrating that the device to be marketed is as safe and effective as another legally marketed device. In the submission, PEREGRINE was compared to other radiation treatment dose calculation systems. What makes it work as well as it does—Monte Carlo mathematics—is significantly different from the means of calculating dose in other systems, but its end use as a planning tool for today's clinics is substantially the same.

PEREGRINE's dose calculation capability will be used with a radiation treatment planning system. A radiation oncologist, medical physicist, radiation therapist, or dosimetrist will use the two together to design a series of radiation treatments that can be reviewed by the patient's physician prior to treatment. PEREGRINE is being used with CORVUS, an inverse planning system created and marketed by NOMOS.

The City of Hope Cancer Center in Los Angeles was the first customer to purchase PEREGRINE, and UCSF, Livermore's long-time collaborator, was the first to take delivery. Numerous other hospitals, including one in Belgium, are beginning the commissioning process. The first patients to benefit from PEREGRINE will likely begin to receive treatment this summer.

Pushing Frontiers

Medical physicist Christine Hartmann-Siantar is program leader for PEREGRINE at Livermore. She says, "Our goal has always been to get what is known as ubiquitous distribution of PEREGRINE. We want to see it in as many clinics as possible, from university centers to community hospitals. This way, every patient will have access to the most accurate radiation dose calculation method."

The Livermore team is now working with NOMOS to add more types of accelerators and more accelerator radiation energy levels to PEREGRINE's database. They are also continuing to work with UCSF, expanding PEREGRINE's capabilities to include electron radiation treatment. Treatment with photons is the most commonly used because photons can travel deep into the body. Electrons are useful for tumors close to the surface because electrons deposit their energy within a few centimeters of the skin.

The PEREGRINE team has also begun a quality assurance project with UCSF to examine the photon radiation dose that exits the body on the side away from the beams. Known as portal imaging, it could be used to check where a small dose goes before the full dose is administered. Portal imaging would also be an excellent tool for periodic use as the full series of treatments are given to assure that the dose being received is the one the radiation oncologist planned.

Hartmann-Siantar joined the Laboratory in 1993 with the goal of applying Livermore's nuclear data and computational know-how to radiation treatment. "I got a chance to work with some of the best computer scientists, engineers, and physicists in the Laboratory," she says. "Without them, PEREGRINE never would have happened."

PEREGRINE team members have won many awards for their work. Hartmann-Siantar added another in February 2000 as one of four first-ever recipients of the Edward Teller Fellowship Award. Working with the team, she is using the fellowship to study how radiation damages DNA. At the time of the award, Hartmann-Siantar said, "I am very excited to have an opportunity to push new frontiers in science." She and her team have already pushed a few, and they aren't stopping yet.

—Katie Walter

Key Words: cancer treatment, Monte Carlo mathematics, PEREGRINE, U.S. Food and Drug Administration.

For further information contact Rosemary Walling (925) 422-4104 (walling2@llnl.gov).

Patents and Awards

Each month in this space we report on the patents issued to and/or the awards received by Laboratory employees. Our goal is to showcase the distinguished scientific and technical achievements of our employees as well as to indicate the scale and scope of the work done at the Laboratory.

Patents

Amorphous-Diamond Electron Emitter

Steven Falabella

U.S. Patent No. 6,204,595 B1

March 20, 2001

An electron emitter comprising a textured silicon wafer overcoated with a thin (200-nanometer) layer of nitrogen-doped, amorphous diamond, which lowers the field below 20 volts per micrometer, compared to uncoated or diamond-coated emitters wherein the emission is at fields of nearly 60 volts per micrometer. The silicon/nitrogen-doped, amorphous-diamond (Si/a:D-N) emitter may be produced by overcoating a textured silicon wafer with amorphous diamond in a nitrogen atmosphere using a filtered cathodic-arc system. The enhanced performance of the Si/a:D-N emitter lowers the voltages required to the point where field-emission displays are practical. Thus, this emitter can be used, for example, in flat-panel emission displays and cold-cathode vacuum electronics.

Method for Vacuum Fusion Bonding

Harold D. Ackler, Stefan P. Swierkowski, Lisa A. Tarte, Randall K. Hicks

U.S. Patent No. 6,205,819 B1

March 27, 2001

An improved vacuum fusion bonding structure and process for aligned bonding of large-area glass plates, patterned with microchannels and access holds and slots, for elevated glass fusion temperatures. Vacuum pumpout of all components is through the bottom platform, which yields an untouched, defect-free top surface that greatly improves optical access through its smooth surface. Also, a completely nonadherent layer, such as graphite, that has alignment and location features, is located between the main steel platform and the glass plate pair. This nonadherent layer makes large improvements in quality, yield, and ease of use, and enables aligned bonding of very large glass structures.

Pedestal Substrate for Coated Optics

Layton C. Hale, Terry N. Malsbury, Steven R. Patterson

U.S. Patent No. 6,206,966 B1

March 27, 2001

A pedestal optical substrate that simultaneously provides high substrate dynamic stiffness, provides low surface figure sensitivity to mechanical mounting hardware inputs, and constrains surface figure changes caused by optical coatings to be primarily spherical in nature. The pedestal optical substrate includes a disklike optic or substrate section having a top surface that is coated, a disklike base section on which the substrate can be mounted, and a connecting cylindrical section between the base and optics or substrate sections. The connecting cylindrical section may be attached via three spaced legs or members. However, the pedestal optical substrate can be manufactured from a solid piece of material to form a monolith, thus avoiding joints between the sections, or the disklike base can be formed separately and connected to the connecting section. The pedestal optical substrate may be used in the fabrication of optics for an extreme ultraviolet lithography imaging system or in any optical system requiring coated optics and substrates with reduced sensitivity to mechanical mounts.

System to Quantify Gamma-Ray Radial Energy Deposition in Semiconductor Detectors

Judith E. Kammeraad, Jerome J. Blair

U.S. Patent No. 6,207,957 B1

March 27, 2001

A system for measuring gamma-ray radial energy deposition is provided for use in conjunction with a semiconductor detector. The detector comprises two electrodes and a detector material; it defines a plurality of zones within the detecting material in parallel with the two electrodes. The detector produces a charge signal $E(t)$ when a gamma ray interacts with the detector. Digitizing means are provided for converting the charge signal $E(t)$ into a digitized signal. A computational means receives the digitized signal and calculates which of the plurality of zones the gamma-ray-deposited energy is in when interacting with the detector. The computational means produces an output indicating the amount of energy deposited by the gamma ray in each of the plurality of zones.

Microfluidic Interconnects

William J. Benett, Peter A. Krulevitch

U.S. Patent No. 6,209,928 B1

April 3, 2001

A miniature connector for introducing microliter quantities of solutions into microfabricated fluidic devices. The fluidic connector, for example, joins standard high-pressure liquid chromatography tubing to 1-millimeter-diameter holes in silicon or glass, enabling milliliter-sized volumes of sample solutions to be merged with microliter-sized devices. The connector has many features, including ease of connection and disconnection, a small footprint that enables numerous connectors to be located in a small area, low dead volume; helium leakproofness, and tubing that does not twist during connection. Thus, the connector enables easy and effective change of microfluidic devices and introduction of different solutions in the devices.

Fluid Intensifier Having a Double-Acting Power Chamber with Interconnected Signal Rods

John C. Whitehead

U.S. Patent No. 6,210,131 B1

April 3, 2001

A fluid-driven reciprocating apparatus having a double-acting power chamber with signal rods serving as high-pressure pistons, or to transmit mechanical power. The signal rods are connected to a double-acting piston in the power chamber, thereby eliminating the need for pilot valves, with the piston being controlled by a pair of intake exhaust valves. The signal rod includes two spaced seals along its length with a vented space there or in between so that the driving fluid and driven fluid cannot mix; the rod performs a switching function to eliminate separate pilot valves. The intake–exhaust valves can be integrated into a single housing with the power chamber, or these valves can be built into the cylinder head only of the power chamber, or they can be separate from the power chamber.

Hybrid Solid State Laser System Using a Neodymium-Based Master Oscillator and an Ytterbium-Based Power Amplifier

Stephen A. Payne, Christopher D. Marshall, Howard T. Powell, William F. Krupke

U.S. Patent No. 6,212,215 B1

April 3, 2001

In a master oscillator–power amplifier (MOPA) hybrid laser system, the master oscillator (MO) utilizes a Nd_3^+-doped gain medium and the power amplifier (PA) utilizes a diode-pumped Yb_3^+-doped material. The use of two different laser gain media in the hybrid MOPA system provides advantages that are otherwise not available. The Nd-doped gain medium preferably serves as the MO because such gain media offer the lowest threshold of operation and have already been engineered as practical systems. The Yb-doped gain medium preferably serves in the diode-pumped PA to store pump energy effectively and efficiently by virtue of the long emission lifetime, thereby reducing diode pump costs. One crucial constraint on the MO and PA gain media is that the Nd and Yb lasers must operate at nearly the same wavelength. The 1,047-micrometer Nd:YLF/Yb:S-FAP [$Nd:LiYF_4/Yb:Sr_5(PO_4)_3F$] hybrid MOPA system is a preferred embodiment of the hybrid Nd/Yb MOPA.

Situ Treatment of Contaminated Groundwater

Walt W. McNab, Jr., Robert Ruiz, Tristan M. Pico

U.S. Patent 6,214,202, B1

April 10, 2001

A system for treating dissolved halogenated organic compounds in groundwater that relies on electrolytically generated hydrogen to chemically reduce the halogenated compounds in the presence of a suitable catalyst. A direct current is placed across at least a pair or an array of electrodes housed within groundwater wells so that hydrogen is generated at the cathode and oxygen at the anode. A pump is located within the well housing in which the cathode(s) is(are) located and draws in groundwater where it is hydrogenated by electrolysis, passes through a well-bore treatment unit, and is then transported to the anode well(s) for reinjection into the ground. The well-bore treatment involves a permeable cylinder located in the well bore. The cylinder contains a packed bed of catalyst material that facilitates the reductive dehalogenation of the halogenated organic compounds by hydrogen into environmentally benign species such as ethane and methane. Also, electrosomatic transport of contaminants toward the cathode also contributes to contaminant mass removal. The only aboveground equipment required is the transfer pipes and a direct circuit power supply for the electrodes. The electrode wells in an array may be used in pairs, or one anode well may be used with a plurality of cathode wells. The direct current flow between electrode wells may be periodically reversed to control the formation of mineral deposits in the alkaline cathode well-bore water as well as to help rejuvenate the catalysis.

Process for Producing Ti–Cr–Al–O Thin Film Resistors

Alan F. Jankowski, Anthony P. Schmid

U.S. Patent 6,217,722 B1

April 17, 2001

Thin films made of titanium–chromium–aluminum–oxygen (Ti–Cr–Al–O) are used as a resistor material. The films are radiofrequency-sputter-deposited from ceramic targets using a reactive working gas mixture of argon and oxygen. Resistivity values of 10^4 to 10^{10} ohm-centimeters have been measured for Ti–Cr–Al–O film less than 1 micrometer thick. The film resistivity can be discretely selected through control of the target composition and the deposition parameters. Ti–Cr–Al–O thin films, unlike other metal oxide films, have been found to be thermodynamically stable when applied as a thin-film resistor. The Ti–Cr–Al–O film can be used as a vertical or lateral resistor (for example, as a layer beneath a field emission cathode in a flat-panel display), or it can be used to control surface emissivity (for example, as a coating on an insulating material such as vertical wall supports in flat-panel displays).

Process for Fabricating Device Structures for Real-Time Process Control of Silicon Doping

Kurt H. Weiner

U.S. Patent 6,221,726 B1

April 24, 2001

Silicon device structures designed to allow measurement of important doping process parameters immediately after the doping step has occurred. The test structures are processed through contact formation using standard semiconductor fabrication techniques. After the contacts have been formed, the structures are covered by an oxide layer and an aluminum layer. The aluminum layer is then patterned to expose the contact pads and selected regions of the silicon to be doped. Doping is then performed, and the whole structure is annealed with a pulsed excimer laser. But laser annealing, unlike standard annealing techniques, does not affect the aluminum contacts because the laser light is reflected by the aluminum. Once the annealing process is complete, the structures can be probed using standard techniques to ascertain data about the doping step. Analysis of the data can determine probable yield reductions due to improper execution of the doping step and thus provides real-time feedback during integrated circuit fabrication.

Delivering Pump Light to a Laser Gain Element While Maintaining Access to the Laser Beam

Raymond J. Beach, Eric C. Honea, Stephen A. Payne

U.S. Patent 6,222,872 B1

April 24, 2001

A lens duct is used to pump delivery, and the laser beam is accessed through an additional component called the intermediate beam extractor that can be implemented as part of the gain element or the lens duct or as a separate component.

Awards

Pioneering advances in astronomy, environmental remediation, human genomics, and physics critical to stockpile stewardship have earned four Laboratory scientists **Edward Teller Fellowships** for 2001. The scientists are **Claire Max, Elbert Branscomb, John Nitao,** and **George Kwei**.

The fellowships recognize and encourage scientific accomplishments and provide fellows with the flexibility to explore new areas of interest by allowing each recipient to do self-directed work for the Laboratory over the next year. This is the second year the fellowships have been awarded.

Max heads the Laboratory's Laser Guide Star Project, central to which is adaptive optics systems, which improve the resolution of ground-based astronomical telescopes. She was also instrumental in creating the new Center for Adaptive Optics headquartered at the University of California at Santa Cruz. The Teller fellowship will enable her to devote herself to a program of intensive cutting-edge exploration in adaptive optics and its emerging applications, to continue mentoring young researchers supporting this work, and to define a strong role for Livermore within the Center for Adaptive Optics and related communities.

Branscomb served as director of the Joint Genome Institute (JGI) in Walnut Creek, California, from its creation until late 2000. Under his leadership, JGI established its Walnut Creek facilities and achieved international recognition for effectively completing its sequencing goals. Branscomb intends to use the fellowship to further explore genes from chromosome 19—one of the chromosomes the Laboratory had responsibility for mapping. He said that he will focus on a large family of genes involved in controlling the expression of other genes in the genome.

With the help of his Teller fellowship, Nitao intends to collaborate with the renowned hydrologist Jacob Bear on a book about subsurface flow and transport for environmental remediation. It will include information on thermal methods for removing contaminants from soil. Nitao is the driving force behind the NUFT code—a versatile computational tool that incorporates the complex physics of multiphase flow and transport of gas, liquids, and thermal energy through a fractured porous matrix. He recently added realistic chemical reactions to NUFT, further expanding the class of problems to which the code can be applied.

Kwei, a physicist, is a leader in neutron-scattering research relevant to stockpile stewardship. He will use his fellowship to write a book on science policy in the White House that addresses how policy advisers work with the President and Congress to set policy. Kwei says that he wants to explain to the general public what science does for them.

The U.S. **Environmental Protection Agency** (EPA) has recognized the Laboratory as a "champion of green government." EPA's **Greening the Government Award** recognizes individuals and groups that go "above and beyond the call of duty in working to improve the environment." The "above and beyond" recognized at Livermore is the recycling of materials from decontamination and demolition projects by the Chemistry and Materials Science Directorate's **Space Action Team** (SPA).

Created some six years ago, the 32-member SPA plans and executes facilities projects Laboratory-wide with the goals of improving efficiency and reducing costs by helping to consolidate facilities and programs.

The EPA award citation reads: "The Space Action Team at LLNL has recycled approximately 90 percent of materials from decontamination and demolition projects at the Lab. Soil, asphalt, concrete, wood, steel, and electromechanical infrastructure and equipment have been recycled during the demolition of 11 buildings and 22 trailers. Soil, asphalt, and concrete are now being used at landfill sites for construction, road improvements, and daily operational needs. LLNL has reduced landfill costs for those materials to zero. Pollution prevention is a guiding principle in all decontamination and demolition projects."

Abstracts

Turning Carbon Directly into Electricity

A team of researchers is investigating direct carbon conversion, an electrochemical process that converts carbon particles directly into electricity without the need for such traditional equipment as gasifiers, boilers, and turbines. The process pushes the efficiency of using fossil fuels for generating electricity closer to theoretical limits than ever before. The direct carbon conversion fuel cell uses aggregates of extremely fine carbon particles distributed in a slurry of molten carbonate at a temperature of 750 to 850°C. In the cell, carbon and oxygen (from ambient air) form carbon dioxide and electricity. The reaction provides up to 1 kilowatt of power per square meter of cell surface area, a rate sufficiently high for practical applications. The process promises to greatly increase the yield of electric energy from each unit of fossil fuel. It uses fuels derived efficiently from any fossil fuel (including coal, lignite, petroleum, natural gas, and even biomass) and significantly decreases the carbon dioxide released into the atmosphere. The process also makes it easy to capture the carbon dioxide for sequestration or other use.

Contact:

John Cooper (925) 423-6649 (cooper3@llnl.gov).

Environmental Research in California and Beyond

Among Lawrence Livermore's many environmental research projects are some that address issues of particular importance to California. Three projects—two involving groundwater quality and a third involving earthquakes—exemplify some of this California-centric work. Study of the migration of MTBE (methyl tertiary-butyl ether) in groundwater in the South Lake Tahoe area revealed that the most likely path of MTBE flow leads directly to water wells. Using a detailed computational model of a site in Orange County, Livermore environmental scientists simulated how viruses and microbes move in groundwater and attach to different geologic media. A region-wide cooperative project called the Bay Area Paleoseismic Experiment (BAPEX) has Laboratory geologists mapping ancient earthquakes to create a 2,000-year chronology of large local earthquakes. The researchers are looking for patterns in timing, location, and magnitude in hopes of providing a framework for more precise earthquake forecasts. Results from all of the California-based projects and others have the potential to benefit not only California but also regions outside the state's borders.

Contact:

Steve Carle (925) 423-5039 (carle1@llnl.gov)—MTBE,
Reed Maxwell (925) 422-7436 (maxwell5@llnl.gov)—viruses, or
Gordon Seitz (925) 423-8469 (seitz3@llnl.gov)—earthquakes.

U.S. Government Printing Office: 2001/683-051-80059

Annual Certification of the Nuclear Stockpile

The review of the status of the U.S. nuclear stockpile, based on the results of ongoing stockpile stewardship work, is a thorough process that involves three national security laboratories, the National Nuclear Security Administration, and the Department of Defense.

Also in July/August

- ***Networked sensors are an emerging means of countering threats and dangers.***
- ***Advances in systems and software improve the accuracy of computed tomography.***
- ***Ongoing studies seek to understand the aging of plutonium.***

Coming Next Month

University of California
Science & Technology Review
Lawrence Livermore National Laboratory
P.O. Box 808, L-664
Livermore, California 94551

Nonprofit Org.
U. S. Postage
PAID
Albuquerque, NM
Permit No. 853