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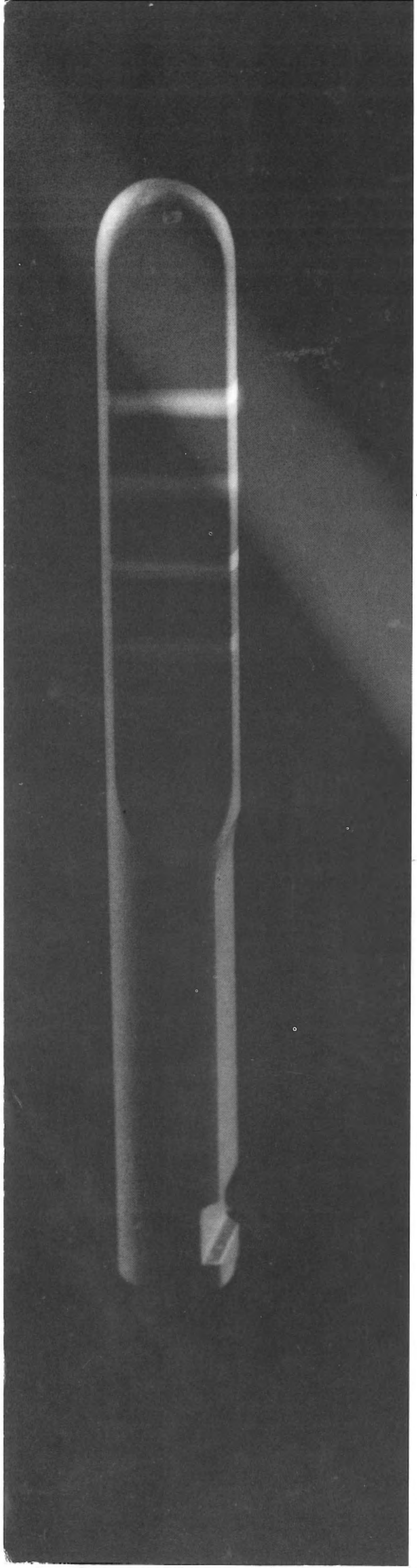
REVIEW

Molecular Marriages for
Improved Chemical Separations

Energy Strategies for a
Greenhouse Future

New Light on
Measuring Temperatures



ON THE COVER

When excited by an ultraviolet laser, thermographic phosphor bands on material samples fluoresce differently at different temperatures. The narrow band of fluorescence can be distinguished from a general luminescent background, such as a flame, enabling researchers to determine the temperature of surfaces that are inaccessible to thermometers or thermocouples. See the article on p. 46.

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REVIEW

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FEATURES

DEPARTMENTS

Oak Ridge National Laboratory is a multiprogram, multipurpose laboratory that conducts research in the physical, chemical, and life sciences; in fusion, fission, and fossil energy; and in energy conservation and other energy-related technologies.

Molecular Marriages for Improved Chemical Separations

By Carolyn Krause

Researchers in ORNL's Chemistry Division have found that the better the marriage between molecules, the better the separation, chemically speaking. So inorganic chemist Bruce Moyer and his colleagues in the Chemistry Division's Chemical Separations Group are trying to be matchmakers—from a molecular point of view.

They are designing, synthesizing, and testing molecules that prefer to "hitch up" with particular metal ions to make possible the selective extraction of these ions from aqueous solution. Principles being applied in this effort lie in the field of "chemical recognition"—the search for ideal reciprocal chemical matches. In this case, the desired matches involve synthetic organic compounds tailored to envelop metal cations (positively charged metal ions) that are either unwanted pollutants or recoverable materials of value. The Separations Group is finding these ideal matches through their efforts at understanding and applying the scientific principles of one of the most selective and versatile of separation processes—solvent extraction.

The group—including crystallographer John Burns and organic chemist Rick Sachleben together with retired ORNL staff members W. J. (Jack) McDowell and Charles F. Baes, Jr.—is proud of several accomplishments. They have patented a two-extractant combination that is potentially more selective than the extractants used by the copper industry for separating copper from other metals in an acid solution. They have also developed highly selective extractants for a number of other metals, including lithium, manganese, zinc, and contaminants such as strontium, cesium, and radium, which are often present in radioactive waste.

By determining the structures of crystalline complexes of extractants (or their chemical analogs) with some of these metals, the group has revealed precise details of the metal-extractant bonding in selected cases. In addition, in seeking to understand principles of solvent extraction, the researchers have developed one of the world's most sophisticated computer programs for modeling the chemical processes of solvent extraction.

Moyer says his group enjoys contributing to scientific knowledge and uses a basic approach in its research. The ORNL group's findings, however, are expected to be used in metal recovery, nuclear separations, and waste treatment.

ORNL has developed highly selective extractants for a number of metals as well as a sophisticated computer program for modeling the chemical processes of solvent extraction.

Solvent Extraction

Solvent extraction is a separation process commonly used by industry for selectively transferring particular metals from aqueous solution into organic solvents. It is used to remove contaminants, such as strontium, from waste streams. It can also separate valuable metals from aqueous sources. For example, much of the world's uranium supply is recovered through solvent extraction. Once extracted into a solvent, the purified metal may be stripped into another aqueous solution for further processing.

According to Moyer, "Our group is interested in determining the chemical reactions underlying extraction of a particular metal from a mixture of metals in a liquid solution. By applying these principles of solvent extraction, we have developed extractants that are highly selective in

About one-fourth of the copper used in the world is obtained from copper ore (an example of which is shown here) by hydrometallurgy. In the commonly used process, copper and other metals are leached out of crushed ore by sulfuric acid. To selectively remove the copper from this impure acid solution, solvent extraction is used. ORNL chemists, including one shown on the back cover, have developed a new extractant for copper.

binding and removing target materials from solution."

Various metals are found in solution throughout the natural world as well as in industrial and laboratory settings. For example, seawater contains salts of metals such as sodium, lithium, magnesium, and potassium. These metals exist in the form of cations. In solution these positively charged ions are balanced by negatively charged ions, or anions, such as chloride, bromide, and sulfate. How do you separate sodium, for example, from a sea-salt solution? Moyer says the separation can be achieved by ion exchange.

"To make ion exchange possible, one exploits the fact that the positive and negative charges in a solution must be balanced."

"To make ion exchange possible, one exploits the fact that the positive and negative charges in a solution must be balanced," he says. "Thus, the removal of cations is accompanied by the return of an equivalent number of positive charges to solution. This separation can be demonstrated by running a sodium chloride solution through a column containing polymer beads of the same type used to soften water. These beads remove the sodium and other cations from the water and replace them with hydrogen ions so that the number of positive charges in the water stays the same. As a result, a solution of sodium chloride is converted to a solution of hydrogen chloride."

Ion exchange is employed in solvent extraction, says Moyer, "except an organic solvent containing an acidic extractant is used instead of polymer beads." In performing solvent extraction, the solvent is dispersed in the aqueous phase (or vice versa). The dispersion of the two liquids can be likened to shaking a bottle of oil and vinegar, he observes. The function of the extractant in the solvent is to bind to a given metal cation, causing its separation from other metals in the aqueous solution, because little or no extraction of metals takes place with most organic solvents that contain no extractant. Acidic extractants are capable of donating protons (hydrogen ions) to the aqueous phase, making possible the transfer of the metal from the aqueous to the organic phase by the process of cation exchange.

Bruce Moyer (right) and Geng Wu, a recent ORAU postdoctoral fellow at ORNL, discuss the reaction of a crown ether with a solution of copper nitrate that is being tested in a calorimeter (shown here). Wu holds a reaction vessel containing the solution. The calorimeter measures heats of reaction, helping the researchers understand the thermodynamic aspects of metal binding by crown ethers.

Extracting Copper from Solution

Copper ore contains many other metals, such as iron, aluminum, sodium, and potassium. About three-fourths of the copper used in the world is obtained by smelting ore—a process known as pyrometallurgy. Approximately one-fourth of the copper is removed by hydrometallurgy, using a process by which copper and other metals are leached out of crushed ore by sulfuric acid. To selectively remove the copper from this impure acid solution, solvent extraction is used. The acid solutions are mixed with a kerosene solution containing an extractant that binds specifically to the copper and removes it from the aqueous solution by cation exchange.

The extractants generally used by the copper industry are hydroxyoximes or hydroxyquinolines, compounds that bond effectively to copper cations. These extractants have the advantage of being relatively inexpensive, says Moyer, but they are not as selective as desired for ideal cost effectiveness because they bind strongly to iron as well as to copper. Overcoming this difficulty is thus one of the keys to improving copper-extraction technology.

ORNL's Separations Group has discovered a combination of two commercially available extractants that is potentially much more selective for copper than the extractant used by the copper industry. One of the extractants is a "crown ether," which binds strictly to copper. The other promotes cation exchange. A crown ether is a large cyclic molecule containing oxygen or sulfur donor atoms linked by hydrocarbon chains; the crown shape of these molecules gives them their name. A patent was obtained on the extractant combination in 1990. But, Moyer says, the copper industry is not likely to replace hydroxyoximes or hydroxyquinolines with the disclosed ORNL extractant combination because this combination is more expensive.

However, he added, recent progress in the Separations Group has pointed to some similar, but much less costly, combinations that bind to copper almost as strongly. The highly selective copper extractant is called tetrathia-14-crown-4. It contains four sulfur atoms bridged by four hydrocarbon links to form a large cyclic molecule, or "macrocycle." Extractants used to foster cation exchange include a sulfonic acid or carboxylic acid, which is dissolved together with the macrocycle in toluene or other organic solvent to form the extraction solvent. Unlike the hydroxyoximes, for example, these cation-exchange extractants are not selective for copper. On the other hand, the macrocycle possesses no cation-exchange ability, so neither extractant can function as a useful copper extractant by itself. Only the combination is effective.

Better Ligands Through Coordination Chemistry

The secret to selective binding, says Moyer, is coordination chemistry—the chemistry of metal ions in their interaction with other molecules or ions. Most extractants are "ligands," ions or molecules containing certain atoms that can form bonds with, or coordinate to, metal cations. Such atoms usually have a partial negative charge and are, therefore, electrostatically attracted to the positive charge of the metal cations. Because they donate some of this negative charge, such atoms are called donor atoms.

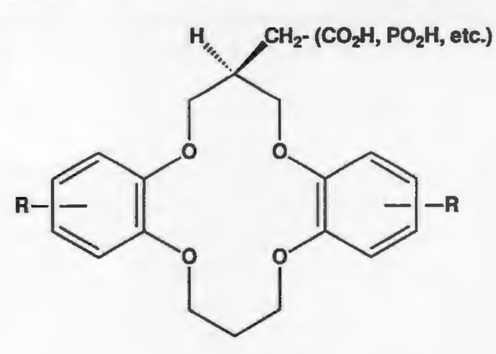
"For good selectivity," Moyer says, "coordinating extractants must have the right donor atoms oriented in the right geometry to bind to a particular metal cation but not to others. Copper in its +2 oxidation state has certain preferences. It likes to have six donor atoms around it, but it usually binds tightly to only four, those occupying sites around its equatorial plane. It likes to bind to any of three common donor atoms—oxygen, nitrogen, or sulfur."

"Coordinating extractants must have the right donor atoms oriented in the right geometry to bind to a particular metal cation but not to others."

A ligand may exhibit "recognition" for copper cations if it can provide a coordination environment that uniquely appeals to copper's preferences. In the case of tetrathia-14-crown-4, the sulfur atoms are linked in a favorable geometric arrangement in which the sulfur atoms are oriented about copper's equatorial plane. This arrangement is also favorable to iron, an important impurity in copper hydrometallurgy. However, iron is rejected by the ORNL extraction system because iron prefers donor atoms of oxygen and nitrogen, which are not present in tetrathia-14-crown-4.

The ORNL combination of extractants uses two commercially available chemicals that Moyer's group has shown to act cooperatively to bind copper selectively. The research group has also developed two-extractant combinations for the solvent extraction of strontium, cesium, and radium ions; they consist of sulfonic or carboxylic

Using a chemical model, Rick Sachleben shows how well single molecules of a synthesized crown ether and a lithium salt fit together. Looking on are Moyer (center) and John Burns. Behind them is a new nuclear magnetic resonance spectrometer for studying the structure of new complexes containing metal-extracting crown ethers.



This lariat ether synthesized at ORNL consists of a relatively rigid macrocyclic framework in which four ether oxygens are held in a planar array by hydrocarbon linking groups. Such a molecule could be the basis for an efficient crown ether extractant of lithium from solution.

acid cation exchangers combined with appropriate substituted crown ethers.

"Ligands have preferences for certain metals," notes Moyer. "We chemists have control over the preference of the ligand, not the metal. We try to design a ligand whose coordination preferences match the coordination preferences of a particular metal. The challenge is to link atoms together in such a way that these atoms are oriented to provide ideal coordination."

Toward a Selective Lithium Extractant

One goal of the Separations Group is to design a single extractant molecule to incorporate both the cation exchange and favorable coordinating properties of two-extractant combinations.

Sachleben has synthesized an impressive series of 13 compounds currently being tested for lithium selectivity. Called "ionizable lariat ethers," these compounds are thought to combine several properties that are favorable for specific lithium coordination. These compounds are called lariat ethers because they have lariat-like shapes—a large ring, or "lasso," with a sidearm. The lariat ethers consist of a relatively rigid macrocyclic framework in which four ether oxygens are held in an approximately planar array by hydrocarbon (CH_2) linking groups, as shown in the drawing on this page.

The most distinctive feature of Sachleben's new compounds is the presence of an acidic carboxylic or phosphinic acid group on a sidearm attached to the macrocycle by CH_2, CH_2CH_2, or OCH_2 groups. Because these acidic sidearms provide a cation-exchange ability, the needed functions of coordination and cation exchange are both present in a single molecule. X-ray studies conducted by John Burns have revealed a wealth of structural details concerning the coordination of the lariat ethers to lithium and sodium cations. Burns' work confirms that the macrocyclic framework indeed provides coordination of the metal cation from the four ether oxygen donor atoms. However, the function of the sidearm is variable, often promoting the formation of chainlike or ringlike structures in the crystal.

Recently, Sachleben perfected techniques for making the lariat ethers highly soluble in organic solvent used in solvent extraction. The technique involves adding large hydrocarbon chains to the lariat ether's benzo groups (those having the six-carbon ring structure found in benzene). As studies in the Separations Group demonstrate, lariat ethers modified in this manner effectively cannot be washed out of organic diluents by alkaline aqueous solutions. This property has paved the way for the beginning of solvent-extraction studies. Preliminary extraction results obtained by Sachleben and Moyer show that the lariat ether dibenzo-14-crown-4-acetic acid has the ability to extract all of the alkali metals, including lithium, sodium, potassium, and cesium. Results for lithium selectivity appear promising, but further work will be needed to quantify the extraction. These new developments concerning the synthesis, structure, and extraction properties of the lariat ether series were announced at the American Chemical Society National Meeting held in April 1991 in Atlanta.

Computers for Chemistry

Chemists are increasingly using computers to model chemical reactions and make calculations to help them design new compounds. In some university, industrial, and government settings, computer modeling is beginning to replace "hands-on" chemical experiments in the laboratory to minimize, for example, the production of hazardous wastes. But Moyer asserts that present-day computers and theory are still inadequate to model most "real-world" problems in practice, although computers and experiments should not be viewed in mutually exclusive terms. Rather, the role of computers lies in helping chemists perform better experiments. Indeed, computer modeling has enabled the Separations Group to understand the chemistry of metal ion coordination and solvent extraction in much greater depth than would otherwise have been possible.

Some of the laboratory research aided by computer modeling involves the study of the structures of extractants and their metal complexes. Burns, a crystallographer, uses X-ray diffraction to determine the minute details of how "macrocyclic" extractant molecules actually bind to metals in crystals. By using computer calculations called molecular mechanics, Burns and Sachleben are able to probe questions concerning, for example, why the lariat ethers assume certain structures in binding alkali metals or which structures might be expected in hypothetical situations.

John Burns checks the alignment of a crystal of a newly synthesized crown ether in an X-ray diffractometer used to study crystal structure.

Insight into the separation ability of extractants has been gained by performing extraction experiments and analyzing the data by computer. "To make these calculations," Moyer says, "we use a program that Charlie Baes has been developing called SXLSQA. It offers the world's best capability in modeling solvent-extraction equilibria." Moyer says that computer modeling helps the ORNL researchers identify the complex molecules formed in various solvent-extraction systems.

"We are world leaders in our ability to selectively remove copper from an acid solution, in our capability to model solvent-extraction chemistry, and in our development of new ionizable lariat ethers," concludes Moyer. Now, the group is focusing on identifying or developing a variety of single extractants that couple with a particular metal and pull it away from a crowd of metals in a solution. With luck, the ORNL group will find molecular matches made in heaven.

Chasing Electrons in Gases and Liquids

By Loucas G. Christophorou

For almost 30 years, our research group at Oak Ridge National Laboratory has been studying the behavior of electrons in gases and liquids. The research has led to many practical applications as well as the exciting capability of altering and controlling the properties of matter for specific technological uses.

Most of our work has focused on slow electrons. What is a slow electron? Imagine a ballerina quickly pirouetting and leaping through a ballroom of slow dancers and out the door. Then think of a ballroom dancer who changes partners every dance and interacts with and embraces each one before leaving through the door at the end of the evening. A fast electron is like the ballerina who has only "glancing" encounters with the dancers, and a slow electron is like the sociable ballroom dancer who has more intimate encounters. A slow electron is so named because of the amount of time required for it to move toward and pass by a target molecule.

Because it travels less than a few thousand kilometers per second, a slow electron is more reactive than a fast electron. Physicists say that a slow electron "sees" more than a fast electron, just as the ballroom dancer sees more of the other dancers than does the ballerina. Slow electrons are also a good subject of study because they are abundant, significant, and challenging.

Why have we studied slow electrons? Because ORNL was once primarily a nuclear research laboratory, it was natural for physicists to study the interaction of ionizing radiation with matter. We originally worked in the Health Physics Division, so we focused on determining the effects of radiation on matter to guide development of radiation dosimeters and to help understand the health effects of radiation. Our group became interested in slow electrons because they are the most abundant species produced when ionizing radiation interacts with matter.

Since then, we have studied slow electrons in gases, liquids, energy-rich "hot" gases, and laser-irradiated fluids. We believe that understanding the ways that slow electrons interact with atoms and molecules is fundamental to understanding the structure of matter and unraveling the secrets of life. We agree with the late Nobel Laureate Albert Szent-Györgyi, who once said, "Electrons are the fluid of life."

The results of these basic studies of slow electrons have led to technological innovations and improvements. Examples are gaseous dielectrics for insulating enclosed electrical lines and equipment to ensure efficient and environmentally acceptable electrical energy transmission and distribution; pulsed power switches, which make possible sharp pulses of electrical energy needed by powerful lasers and sources of microwaves for satellite communications and defense applications; and advanced particle detectors for radiation monitoring and for particle characterization and positioning, as in the massive detectors being designed for the Department of Energy's Superconducting Super Collider.

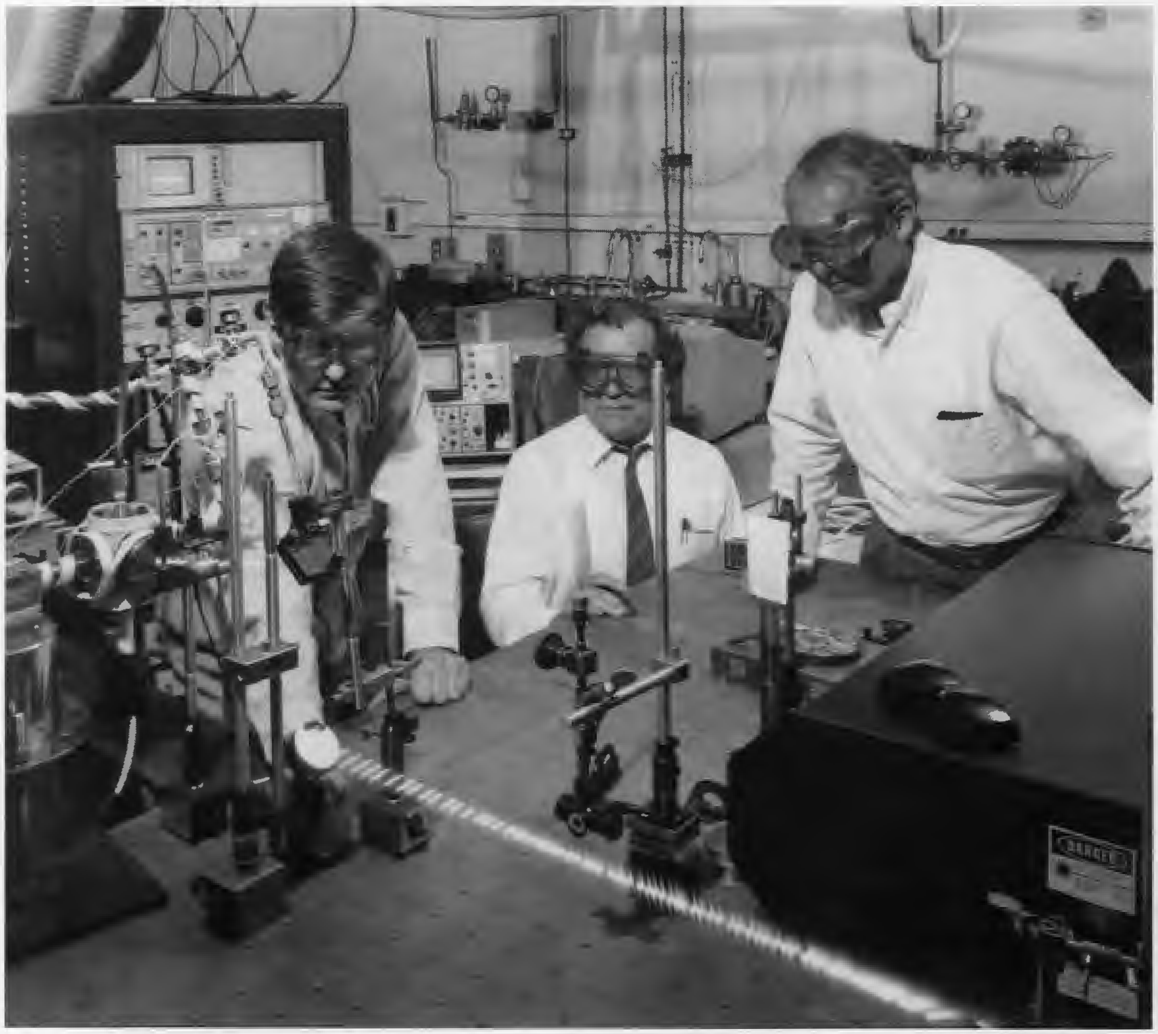
ORNL research results also have contributed to the development of gas-discharge lasers, ultrasensitive analytical instruments, radiosensitizing agents, and plasma chemistry processing. Some of the practical uses of our research results are presented here.

Perhaps our most important contribution to the knowledge base in practical areas has been our organization and sponsorship of six International Symposia in Gaseous Dielectrics, one of which is held every few years in Knoxville, Tennessee. This is the nation's premier meeting on this subject.

One of our most exciting results recently has been our ability to switch, modulate, and control the properties of matter at will. We have developed gaseous and liquid media that conduct

ORNL's basic studies of electron behavior in matter have spawned many applications.

Homer Faidas (left) makes an adjustment as Dennis McCorkle transfers trimethylsilane into a drift velocity cell for studies of electron transport properties in liquids.



Homer Faidas (left), Loucas Christophorou, and Dennis McCorkle align the laser beam for a laser-induced photodetachment experiment for studying the behavior of free electrons in liquids.

electricity at low electric fields but become electrical insulators at high fields. We have developed a gas that conducts electricity when it is warm but becomes an insulator when it is cold and other gases that do the reverse. The ability to change one property of a gas or liquid to its opposite at the molecular level makes possible the development of fast switches.

In this research, I have worked over the years with many colleagues, students, postdoctoral fellows, visiting scientists, and support staff members. I am particularly grateful to these contributors at ORNL: Don Bouldin, James G. Carter, Panos G. Datskos, Homer Faidas, Guy D. Griffin, Scott R. Hunter, Randy D. James, Richard Mathis, Dennis L. McCorkle, Marshal Pace, Bob Y. Pai, Lal A. Pinnaduwage, Isidor Sauers, and J. Phil Sawyer.

Producing and Controlling Slow Electrons

How are slow electrons generated in gaseous and liquid matter? Several mechanisms make them available for study. When high-energy particles bombard atoms and molecules in liquids and gases, they may transfer some of their energy to these species, converting them into positive ions (charged atoms or molecules having a deficiency of electrons) and free electrons. Slow electrons also can be generated by atoms or molecules after absorption of photons of light; they can be released from atoms and molecules by "photoionization" or from negative ions by "photodetachment." They can also be injected into gases and liquids from surfaces by various means (e.g., photoinjection, where electrons are produced from a metal surface bombarded with photons).

Other sources of slow electrons are collisions of excited atoms with unexcited atoms, negative ions with neutral atoms, and electrons with neutral atoms or ions. While traveling through a gas or liquid, slow electrons may lose their energy and slow down even more as they collide with atoms and molecules in matter. Little energy is transferred if the collision is elastic, but in inelastic collisions, various amounts of electron energy will be transferred, depending on the process. These processes can slow electrons from as high as several million electron volts (eV) to under 100 eV and all the way down to thermal energies (~0.04 eV).

We call ourselves magicians because of our ability to control the number and energies of electrons in electrically stressed matter—fluids subjected to an electric field. Examples of such fluids are gas discharges and gaseous and liquid dielectrics for insulating enclosed power lines. (An electric field is a fundamental field of nature that causes a charged body to be attracted to or repelled by other charged bodies; it can be produced by applying a voltage between two electrodes.)

Just as a magician can make a rabbit disappear,

Jim Carter (left) and Lal Pinnaduwage adjust the picosecond pulse-width nitrogen laser system for studies of the phenomena of electron attachment and detachment in dielectric liquids.

In 1978 Isidor Sauers used this time-of-flight mass spectrometer to study the ions formed by the interaction of low-energy electrons with dielectric gas molecules.

we can make free electrons in a gas disappear. Our approach is twofold: (1) choose a gas containing atoms or molecules that easily capture electrons at low energies and (2) select a correct electric field strength or a buffer gas to slow down free electrons, thus increasing the probability that they will be captured by the atoms or molecules in the gas. Through these choices, we can control electron number densities and energies and convert atoms and molecules to negative ions and back again. In addition, we can slow down electrons to the very low energies of the surrounding atoms and molecules (thermalization) or to energies above those of the surrounding species (steady state). Finally, as will be described later, we can make certain fluids switch their properties (e.g., from an insulator to a conductor and vice versa).

Gaseous Dielectrics for Power Transmission and Distribution

In high-voltage conductors such as transmission lines, electricity travels inside a "pipeline" because the conductor that contains the moving energy is insulated from the ground. The chief role of insulation is to inhibit motion of the few free electrons that can trigger "breakdown," a process in which these electrons are energized enough by high-voltage fields to free more electrons from molecules, thus rupturing the pipeline insulation. When breakdown occurs, equipment is damaged and the power system may go out of service, causing blackouts over large areas.

For high-voltage transmission lines, the most common insulation is simply air. Because air inhibits breakdown only if the high-voltage conductor is a long distance from other objects, high-voltage lines must be strung between towers and tall poles to separate them sufficiently from the ground.

This widely used insulating method for power lines has several disadvantages. It requires considerable land and detracts from the beauty of many landscapes. It allows emission to the environment of low-frequency electromagnetic radiation, which has been suggested as a cause of adverse health effects, such as cancer and birth defects. It also generates corona noise, which causes electrical interference. Its energy losses caused by electrical resistance make it inefficient—5 to 10% of the electrical energy transmitted this way in the United States is dissipated to the environment.

These disadvantages can be overcome by using gaseous dielectrics—certain gases such as sulfur hexafluoride (SF_6)—to insulate electric power transmission lines and other equipment, such as circuit breakers and transformers. Because these insulating materials are more effective than air and because they can be used at pressures higher than one atmosphere, they allow utilities to use more compact equipment and enclosed underground or aboveground cables that are aesthetically more acceptable and can operate at higher voltages. Less land is needed, the cables are hidden, no electromagnetic radiation is emitted, and the higher voltages save energy because they permit a lower current, thus reducing energy losses.

Compressed-gas insulated transmission (CGIT) lines or cables have been in service since 1968. In 1985 more than 13 km (circuit length) of lines and cables were in operation worldwide at voltages from 145 to 550 kV. As of 1982, the lengths of CGIT links installed around the world were 5584 m in North America, 3071 m in Asia, and 4485 m in Europe, Africa, Central and South America, Australia, and other places.

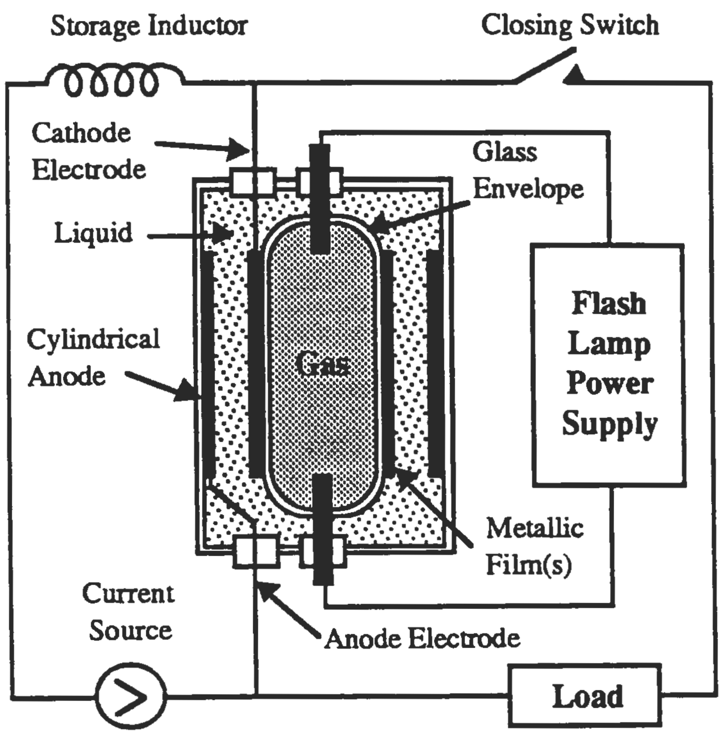
We have studied SF_6 in detail and developed several alternative dielectrics that are improvements over SF_6. To remove the troublesome free electrons near a high-voltage conductor that could cause breakdown, we selected molecules that are particularly effective at capturing slow electrons. We found that slow electrons are easily attached to perfluorocarbon gases. Electrons near a conductor, however, must be slowed down so they will be captured by the perfluorocarbon molecules. Therefore, we looked for a second gas to slow down these electrons. The "buffer" gases we found to be effective include, among others, nitrogen and carbon dioxide. We then identified the mechanisms by which these gases retard electron motion.

Our research turned up combinations of gases that give a dielectric strength (resistance to breakdown) more than twice as high as that of SF_6

alone. Thus, use of these gases as insulators of enclosed power lines could permit voltages perhaps as high as 1.5 MV (compared with a maximum of 765 kV for aboveground power lines). As a result, the current would be much lower and the resistive energy losses would be less than 3% of the transmitted electric energy.

Since the 1960s SF_6 has been used as a gaseous dielectric for transformers and enclosed electrical transmission and distribution lines. However, shortly after the discovery in the 1970s that oils containing polychlorinated biphenyls (PCBs) that were used in electrical equipment are potentially carcinogenic, environmentalists started to question the safety of other chemicals used in electrical equipment.

In the 1980s, our group began studying the biological and environmental effects of SF_6 and other dielectrics. SF_6 itself is not toxic, but Guy Griffin of the Health and Safety Research Division was the first to prove that some gaseous byproducts of sparked SF_6 are toxic to living cells. We tested other dielectrics and found that mixtures containing SF_6 and nitrogen are much safer than SF_6 alone and work just as well as insulating gases.



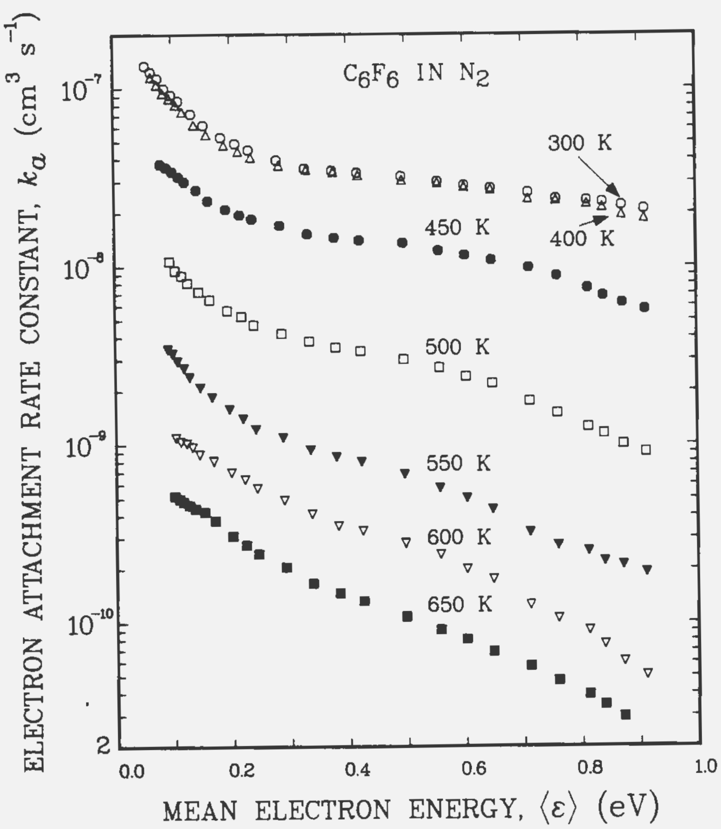
ORNL research has aided the development of the dielectric liquid pulsed-power switch, shown in this schematic. In this device, a liquid dielectric can be changed from an insulator to a good conductor by photoinjecting electrons into it. This switch can be powered by a flashlamp, which bombards a metal with photons, resulting in the release of a flood of electrons into the liquid dielectric.

Pulsed Power for Lasers

It can take tenths of a second to deliver electrical energy to be stored in an inductive coil, which packs a lot of current into a small volume. This storage can be achieved under low electric fields applied across a gaseous (or liquid) conducting medium. Then this stored energy can be delivered within a billionth of a second as a powerful electrical pulse using a fast-opening switch. As a result, a high induced electric field is generated that stresses the medium. Such pulsed power is needed for switching on powerful pulsed lasers (e.g., for laser fusion and particle-beam weapons) and pulsed sources of microwaves (e.g., for satellite communications and defense applications).

We have developed a diffuse-discharge pulsed-power switch using a gas whose electrical properties change according to the strength of the applied electrical field. At the flick of a switch, we can switch the properties of matter.

Basically, we have developed a gas that is a good conductor of electricity in low electric fields. At these applied fields, the gas is ionized by external sources such as light or high-energy



Some gases are insulators when cold and conductors when warm or hot. An example is hexafluorobenzene (C_6F_6) in a buffer gas of nitrogen (N_2). The drawing shows the electron attachment rate constant as a function of mean electron energy for various temperatures of the combined gases.

particles, freeing electrons that move quickly through the gas and along a circuit to the inductive coil for storage.

When the energy stored in the inductive coil is drawn out as a quick, powerful pulse, a high voltage is induced that could cause the gas to break down. But this gas is special: under a high induced voltage, it turns from a conductor to an insulator!

How does this happen? In low electric fields, the electrons present in the gas have low kinetic energies for which the gas is "transparent"—that is, the electrons drift very fast and are not captured by the molecules making up the gas. Hence, electrical conduction is maximized. When the stored energy is transferred to a load (e.g., activation of a laser), the electric field is high.

Such a high field causes the free electrons to gain kinetic energy. However, the gas molecules can capture the more energetic electrons very efficiently. Also, at these high fields, the electrons drift slowly, having a higher probability of being efficiently captured and producing slowly moving ions. Hence, under the high induced electric fields, the gas is now a good insulator.

When the electric field is switched from high to low, the gas again becomes a conductor. The two multicomponent gases that we have found to work in this way combine argon (Ar) with two perfluorocarbons: Ar/C_2F_6 and Ar/C_3F_8.

We also have introduced the development of a dielectric liquid pulsed power switch (see figure on p. 13). In this device, a liquid dielectric can be changed from an insulator to a good conductor by photoinjecting electrons into it. This switch can be powered by a flashlamp, which bombards a metal with photons, resulting in the release of a flood of electrons into the liquid dielectric.

We have developed gases that could be used for temperature-controlled switches. They are conductors when cold (because the electrons are not captured but instead remain free) and insulators when warm (because, in that temperature range, electrons become attached to nearby molecules, forming slowly moving negative ions). One such gas is a compound of carbon, chlorine, and fluorine ($CClF_3$). Other gases, such as C_6F_6 (see figure above) and cyclo-C_4F_6, work in reverse: they are insulators when cold and conductors when warm or hot! By changing the temperature of these gases, we can switch or modulate their dielectric properties.

Fast Gases for Detectors

We are interested in gases that produce or ease the flow of fast electrons, as well as gases that slow down and capture electrons. Our group was the first to develop fast gases. Other groups are now involved in developing them for various types of detectors and other uses.

Our studies of fast gases are expected to contribute to the development of particle detectors for DOE's Superconducting Super Collider (SSC), the accelerator expected to provide more detailed information on the building blocks of atoms. For the SSC, a fast gas is needed because a massive number of particles must be detected each second as they are produced by the proton-to-proton collisions in the accelerator's oval track. The particle detector will detect muons indirectly by collecting and counting electrons in the fast gas.

These electrons are produced by interactions between the gas molecules and muons, semistable elementary particles having positive and negative charges that are generated by proton collisions in the SSC. In a fast gas in a particle detector, electrons drift as fast as possible under a given voltage toward an anode, where they are counted by measuring electrical pulse heights. The numbers of the electrons counted by specific and complicated detector arrangements indicate the identity, speed, and direction of each muon entering the detector.

A fast gas is usually a multicomponent gas. The components must work together to maximize electron drift, minimize electron diffusion, reduce electron energies, and maximize electron production for the electric fields used in practice. We have identified a number of multicomponent gases that are good candidates for fast detector gases, and we have determined the correct electric field to be applied to each to increase electron drift velocities.

In 1979 we found that a very effective fast gas is a combination of argon and carbon tetrafluoride (CF_4). Argon atoms do not capture electrons and, at low energies (~0.5 eV), argon gas is transparent to electrons—that is, electrons having energies around 0.5 eV move easily through argon gas. We added CF_4 to argon because this compound scatters faster electrons and keeps them in an energy range where they drift quickly.

We are proposing to the SSC detector developers that they consider Ar/CF_4 combined with carbon dioxide (CO_2) as a fast detector gas, which is also "cool"—that is, under operating electric fields, the electron energies and diffusion are small. This effect improves the detector's particle-positioning capability and allows for more accurate determination of the particle's momentum. CO_2 can also be ionized by excited argon atoms (by Penning ionization), and the freed electrons increase the detector signal.

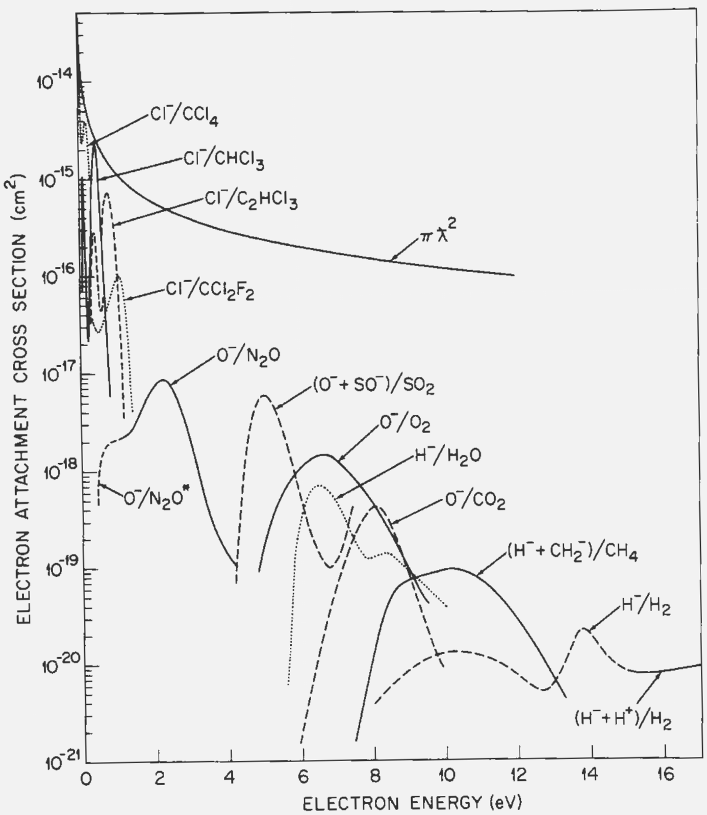
The results of our basic research have also been used to develop particle detectors filled with fast, room-temperature liquids for the SSC and other types of detectors.

Radiosensitizing Agents

Our physics studies have contributed to basic knowledge in the life and environmental sciences. We have provided basic information that has guided the development of ultrasensitive chemical detection methods. We have shown that environmental halocarbons easily break down in the presence of slow electrons, and we have quantified their fragmentation patterns. We have improved understanding of the electron-accepting capacities of biomolecules. An example is the development of radiosensitizing agents.

It has been found that certain drugs injected into tumors make them more sensitive to radiation; thus, use of such drugs could reduce the amount of radiation needed to destroy a tumor and protect normal tissue from unnecessary radiation damage.

Further studies have found that chemicals that tend to capture slow electrons (including those produced by ionizing radiation in tissue) are often good radiosensitizing agents. Because of our reputation for studying electron-capturing components of liquids and gases, we were asked to identify biomolecules that capture electrons. We suggested several compounds, including



Slow electrons react more efficiently with host molecules than do fast electrons, as shown by these measurements of electron-attachment cross sections as a function of electron energy for various molecules. $\pi\lambda^2$ is the maximum possible electron-capture cross section.

perfluorocarbons, that we consider good candidates for radiosensitizing agents.

Negative Ions and Explosives

We have discovered an interesting feature of the so-called indirect, or capturing, collision in which a molecule captures a slow electron. In this case, a slow electron may enter an empty orbital of a molecule, occupying it for a brief time (ranging from 10^{-15} to $>10^{-3}$ s) and forming a transient negative ion state. The electron then leaves the molecule, often with only a fraction of its initial energy.

Molecular nitrogen gas (N_2) is a good example of a transient short-lived negative ion. In this case, a 2.3-eV electron can be captured by N_2, forming a negative nitrogen ion for only 5×10^{-15} s. The electron then detaches itself from the nitrogen ion, often as a slow electron, which has less energy than it had when captured by the molecule.

Our research group discovered and studied the negative ion states of many organic and other polyatomic molecules formed by indirect collisions with slow electrons. In our pioneering research, we found that negative ion states of certain molecules can be an effective means of removing slow electrons from a liquid or gas.

The nuclei of molecules are surrounded by an infinite number of orbitals that are either empty or occupied by one or more electrons. A free electron can enter and occupy an empty molecular orbital if its energy matches that of the orbital. We have found that, the lower the energies of the empty orbitals are, the higher the probability of electron capture by an atom or molecule in a gas or liquid.

Some of the ions produced by electron capture break apart easily, forming "fragment negative ions." In fact, we found that many polyatomic molecules are extremely fragile in the presence of slow electrons. Other negative ions formed by electron capture, called parent negative ions, can be quite stable.

What is the difference between parent negative ions and fragment negative ions? We have found that parent negative ions are usually formed when they are in the lowest-lying negative ion states—that is, the energies of the orbitals being occupied by electrons approach 0 eV. The negative ion states of fragment negative ions have been found to range up to ~15 eV.

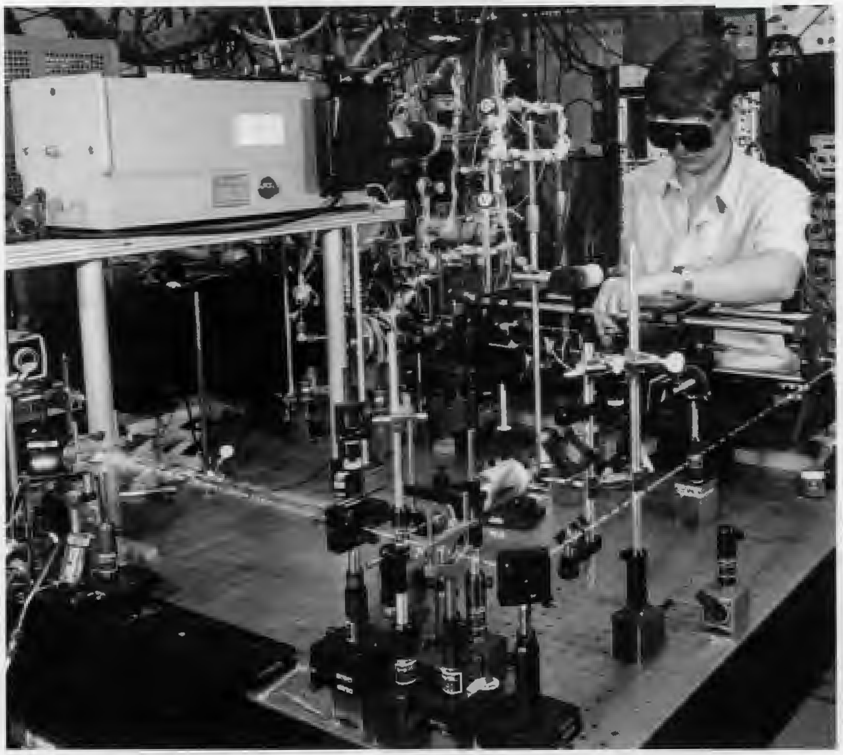
Parent ions may have practical uses as "taggants" to indicate the presence of explosives. For example, negative ions of a perfluorocarbon might be a good marker for an explosive because they do not break down in the presence of slow

Carter (left), Scott Hunter, and Christophorou work at the experimental apparatus used to measure electron transport properties in high-pressure, high-temperature gases and gas mixtures.

electrons; are not present in clothing, luggage, and other common items; and escape to the air, where they could be collected and detected by a mass spectrometer (which separates substances by mass and charge). Because of the need to detect explosives at airports and other public places to reduce the threat of terrorism, governments of many nations are considering requiring manufacturers to add taggants to their explosives.

What are some results of our other basic studies? In our electron attachment cross-section studies, we have determined the probability that electrons of various energies will be captured by a host of molecules and atoms (see figure on p. 16). These include carbon tetrachloride and other freons, nitrous oxide, sulfur dioxide, methane, carbon dioxide, water, and negative ions of chlorine, hydrogen, and oxygen.

We have found that interactions of slow electrons with molecules depend strongly on the internal energy content of the molecules. Excited species were found to react with slow electrons much more strongly than unexcited species. As the vibrational energy of the molecule increases, dissociative attachment of electrons increases and nondissociative attachment decreases —that is, the transient negative ion breaks down faster into fragments or it releases, or autodetaches, the attached electron faster as its internal energy is increased. We found that molecules excited by the absorption of light were more likely to scatter electrons than were unexcited, ground-state molecules.



To achieve the desired wavelength of laser light for a multiphoton ionization experiment on liquids, Homer Faidas optimizes the output of a frequency doubler.

to vibrationally excite, or pump, the CO_2 molecules in the lasing state is to transfer energy to them from vibrationally excited nitrogen gas (N_2*). The nitrogen is excited by electrons photoinjected into the gas and given appropriate energy by application of a suitable electric field.

Basic studies made a contribution to increasing the efficiency of CO_2 lasers by determining the strength of the electric field needed to maximize the probability that nitrogen molecules would capture electrons and form N_2^{-*}, which upon decay efficiently produces vibrationally excited nitrogen molecules (N_2*) for pumping the CO_2 lasing state. In our studies, we have found that vibrational excitation of species in a gas or liquid has a profound effect on the movement of electrons through the medium to a collector, as in a detector.

We discovered that the probability of capture of slow electrons by electronically excited molecules can be millions to billions of times larger than for the ground-state species. A molecule is electronically excited when one or more of its electrons absorb energy and jump to a higher energy state (an orbital farther from the nucleus). Electrons may be easily attached to electronically excited molecules such as the metastable ($>10^{-5}$ s), long-lived excited states of the thiophenol (C_6H_5SH) molecule and the short-lived ($<10^{-8}$ s) excited electronic states of the triethylamine [$(C_2H_5)_3N$] molecule.

Vibrational Excitation and Efficient Lasers

Some diatomic gases become vibrationally excited following capture of an electron. This phenomenon has been important in making the CO_2 laser more efficient.

When CO_2 molecules vibrate, they give off infrared light. It has been found that the best way

Dense Fluids and Conduction

We have studied electron behavior and interactions in dense fluids—high-pressure gases and liquids—and have found interesting relationships between fluid density and electron behavior. For example, as the medium density increases in gases such as ammonia, carbon dioxide, and helium, electrons can become localized—that is, the probability that they exist in a certain region is high and their mobility is low (they move slowly, like ions). In argon, xenon, and other high-pressure gases having spherical-type molecules, as the medium density increases, the electrons can become delocalized, or quasifree, if a conduction band develops. We determined the density at which certain fluids develop conduction bands.

Conduction bands have long been known to exist in electrically conducting metals, but they also can be found in dielectric liquids. In fact, we found that quasifree electrons can move faster in liquids having conduction bands than in low-pressure gases.

One research project of the future may be to determine if DNA has a conduction band. If so, then electron transport and interactions along the DNA conduction band may be linked to chemical changes that could lead to genetic mutations or cancer. If such a connection is made, basic mechanisms could be found for understanding and testing the effects on DNA of radiation and chemicals. Such a test might complement, for example, the Ames test in determining whether a chemical is potentially mutagenic or carcinogenic.

For the future, we hope to conduct research to better understand electron-excited molecule interactions, the behavior of electrons in gases and liquids, and the liquid state of matter. We hope to contribute to the development of liquid-state electronics, the use of electrons to determine liquid structure, elucidation of the structure of biological liquids, development of separation processes to produce ultrapure liquids, and identification of fundamental processes or mechanisms that can be employed as radiation-effects signatures—that is, indicators of early radiation damage.

Our work demonstrates the importance of basic research. Such research has provided fertile ground for the development of useful technologies.

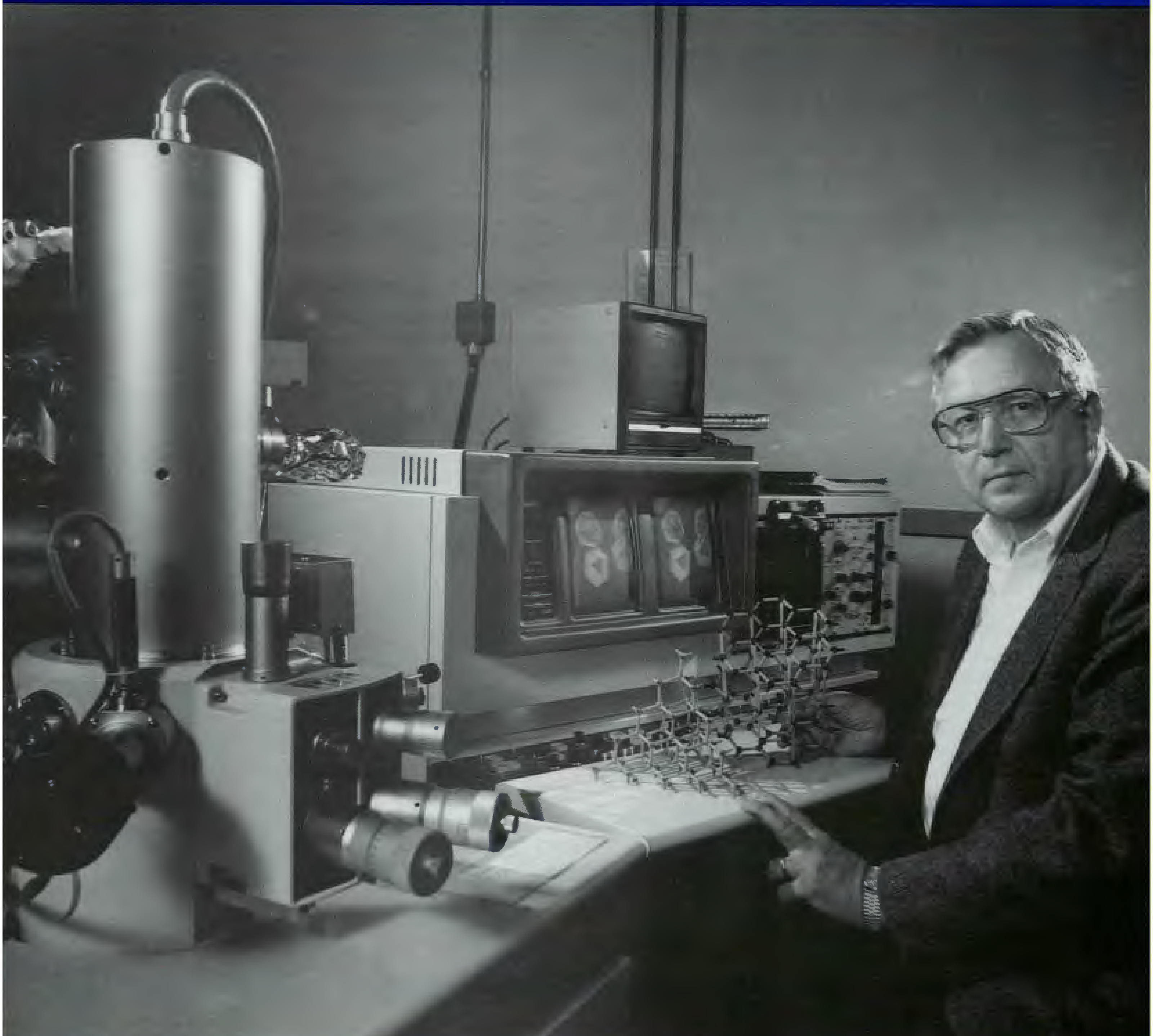
Biographical Sketch

Loucas Christophorou has been leader of the Atomic, Molecular and Radiation Physics Group in ORNL's Health and Safety Research Division since 1966, two years after he came to ORNL. He is a senior corporate fellow of Martin Marietta Energy Systems, Inc., and chairman of ORNL's Corporate Fellow Council. Since 1964 he has served as a Ford Foundation professor of physics at the University of Tennessee (UT) at Knoxville. He was the first co-chairman of the UT-ORNL Distinguished Scientist Program.

Christophorou is the author of two books, *Atomic and Molecular Radiation Physics* and *Electron-Molecule Interactions and Their Applications*, and 260 scientific journal papers. He is the most frequently cited researcher at ORNL (an average of more than 300 citations per year in technical journals). He has delivered 75 major university lectures. A native of Cyprus, he earned his Ph.D. degree in physics in 1963 from the University of Manchester in England and has an honorary degree from the same institution. He has been chairman of six International Symposia in Gaseous Dielectrics, held every few years in Knoxville and recognized as the premier national meeting on this subject. A recent recipient of the Humboldt Award, he is now teaching and conducting research for a year at the Free University and the Hahn-Meitner Institute in Berlin, Germany.

Diamond Films Are (Almost) Forever

By Alexandra Witze



Bob Clausing points to a diamond·model and tilts a graphite model at the Hitachi S-800 scanning electron microscope. This instrument is used to make micrographs (displayed on screens) showing the structure of diamond films made by chemical vapor deposition.

Somewhere on the second floor of an ordinary-looking building at Oak Ridge National Laboratory, Bob Clausing, Linda Horton, and Lee Heatherly of the Metals and Ceramics (M&C) Division are making diamonds. With only heat, gas, and a plate to grow them on, they create the sparkling crystals that have fascinated people for centuries. But Clausing warns, "These diamonds won't fit in your wedding ring." They are as genuine as the ones formed deep in the earth, but they are grown as thin films, which have practical uses other than for jewelry.

Diamond is one of the most extraordinary natural materials. Because it is unsurpassed in hardness, diamond coatings can be used to make scratch-resistant lenses and wear-resistant cutting tools. Its room-temperature thermal conductivity makes it useful for dissipating heat from computer chips. It is a good electrical insulator, but it can be doped with other substances, such as boron, to make superior semiconductors. And its popularity as a gemstone ensures our interest in all of its various applications.

Diamonds from Graphite

The history of diamond research dates from 1797. In that year, the English chemist Smithson Tennant showed that diamond produced carbon dioxide when burned in oxygen. Thus diamond was proven to be a form of carbon, one of three crystalline forms of the element. The other two forms are graphite and the recently discovered fullerenes, including the famous "bucky balls" (see sidebar on p. 28). For over a century scientists, like the medieval alchemists trying to transmute ordinary materials into gold, attempted to convert gray, sooty graphite into clear sparkling diamonds. The difficulties they encountered resulted from the different crystal structures of the two substances.

The atoms in graphite are arranged in hexagonal layers. The bonds between atoms in each layer are strong, but the bonds between layers are weak; as a result, the layers slide against each other easily. This slipperiness makes graphite an effective lubricant. Diamond, on the other hand, is made of atoms tightly fixed in a symmetrical arrangement. Each carbon atom is bonded to its neighboring atoms very strongly in the shape of a tetrahedron, a five-atom pyramid with four atoms arranged at equal distances and equal angles from a central atom. This arrangement makes diamond the hardest of all natural substances.

Graphite can be converted into diamond by squeezing the atoms into a different structure. The first modern attempts to synthesize diamond used high pressures and high temperatures to simulate the natural diamond-forming conditions in the earth's interior. In 1955, a group from General Electric Research Laboratory made diamonds from graphite, using a pressure of 55,000 atmospheres and a temperature of 2000°C. Today the process has become commercial but is restricted by the high cost of maintaining the specialized engineering equipment.

Chemical Vapor Deposition

About this time, Soviet and American researchers independently discovered another method for producing diamonds. The process, known as chemical vapor deposition (CVD), can occur under low pressures, as low as a fraction of an atmosphere. Although graphite is the stable form of carbon under these conditions, diamond can be made through a "metastable" process. CVD diamonds grow out of a hydrocarbon gas, such as methane, under conditions that favor the formation of diamond over graphite.

When first applied to making diamond, the CVD process was very slow and not commercially competitive with high-pressure, high-temperature compression. In addition, both graphite and diamond were deposited, so the graphite had to be frequently cleaned off the surface. For several decades, CVD was impractical for commercial diamond production.

Then, in the late 1970s, Soviet scientists B. V. Derjaguin and D. B. Fedoseev discovered that the presence of atomic hydrogen greatly speeded up diamond deposition. The various roles of hydrogen in diamond growth are still not clearly understood, but, for one, it appears to reduce the amount of codeposited graphite. Derjaguin and Fedoseev also discovered that "activating" the hydrocarbon gas, through a hot filament and an electric discharge, increased the rate of diamond growth to the order of a micrometer, or one ten-thousandth of an inch, per hour. CVD has now become efficient enough to compete for some applications with the high-temperature, high-pressure process for forming diamonds.

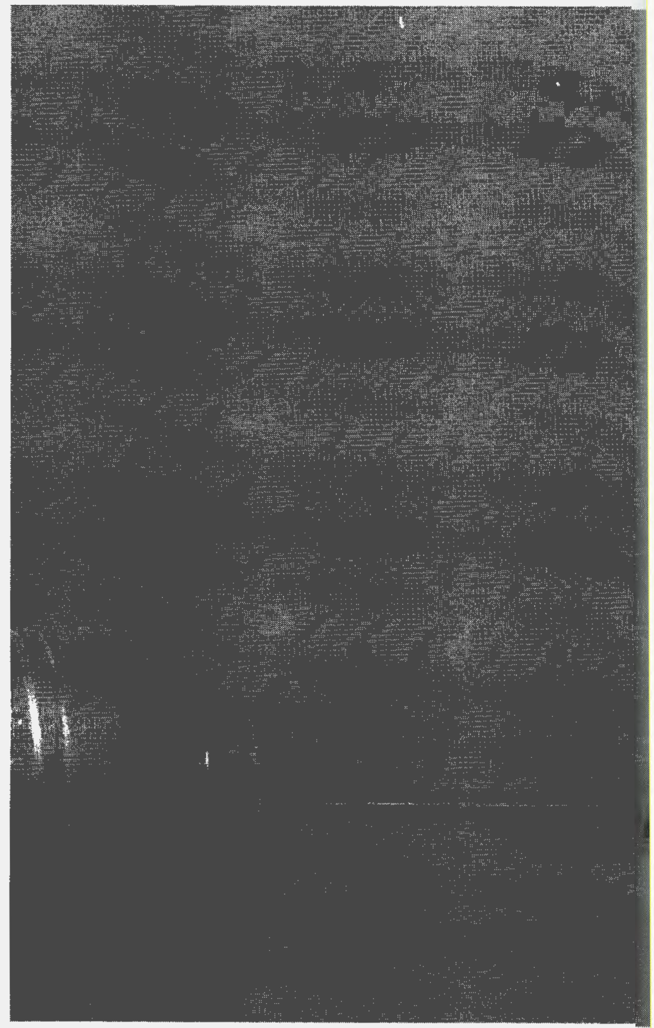
ORNL researchers are making and studying thin diamond films that have uses as abrasives, optical devices, and cutting tools and that could advance the electronics industry.

Diamondlike Materials

Clausing says he "got into the diamond-growing business by a very circuitous route." He and Lee Heatherly, also of the M&C Division, were working with the Fusion Energy Division, looking at plasma interactions with materials. They were attempting to clean walls of fusion devices to remove impurities from the wall closest to the hot plasma of fusion devices. Because materials from the wall contaminated the plasma and reduced its usefulness for fusion studies, Clausing said, "we added carbon to the wall to make a metal carbide. We then learned that coating the wall with a hard carbon material kept the plasma cleaner than did the other techniques we tried. Soon we began to make carbon films. We subsequently realized that we were making the same kind of films that other people were making and calling 'diamondlike.'"

Diamondlike materials are similar to true diamonds; they can be made relatively clear, can be harder than sapphire but not as hard as crystalline diamond, and can be used in some of its applications. They can be easily distinguished from real diamonds by using Raman spectroscopy and electron or X-ray diffraction. Diamondlike materials are amorphous (their atoms are not arranged in any definite crystal order), and they cannot be substituted for true diamond films.

Three years ago, Clausing and his co-workers decided to try something different. "One reason we were making diamondlike films is because they were very hard and scratch-resistant. We decided that we should try to see whether the CVD diamond technology could do an even better job than the material that we were using. We were almost immediately successful in growing CVD diamond films."



ORNL's Hot-Filament CVD Procedure

Clausing's laboratory uses a hot-filament CVD procedure for diamond deposition. The hot filament (around 2000°C), which is made of tungsten carbide, is used to "activate," or dissociate, the hydrocarbon gas into hydrogen, carbon, and hydrocarbon radicals. The substrate, the plate on which the carbon from the gas is deposited as diamonds, can be made of many materials. Silicon is often the most convenient, but natural diamond and molybdenum are frequently used. Materials that are stable and do not react rapidly with carbon or atomic hydrogen at the temperature of deposition, usually 700–1200°C, can be used. The gas is typically 1% methane in hydrogen, at a flow rate of 50–100 cm^3/min. Other hydrocarbon gases may also be used. For best-quality films, the rate of diamond deposition is around 1 µm/h at present. Faster growth rates result in a loss of quality and uniformity of the film.

Other processes for growing diamonds differ in the way they activate the gas. Microwaves are commonly used in place of a hot filament to dissociate the gas. More recent approaches use plasma torches or oxyacetylene flames. In 1988 a

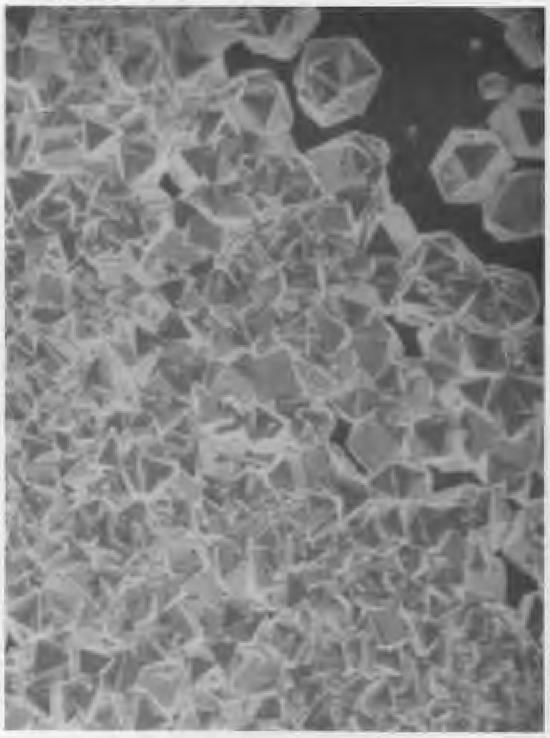
Lee Heatherly studies a hot tungsten carbide filament used in growing thin diamond films by the chemical vapor deposition process.

Japanese researcher produced a diamond film simply by holding a welder's torch over a molybdenum disk.

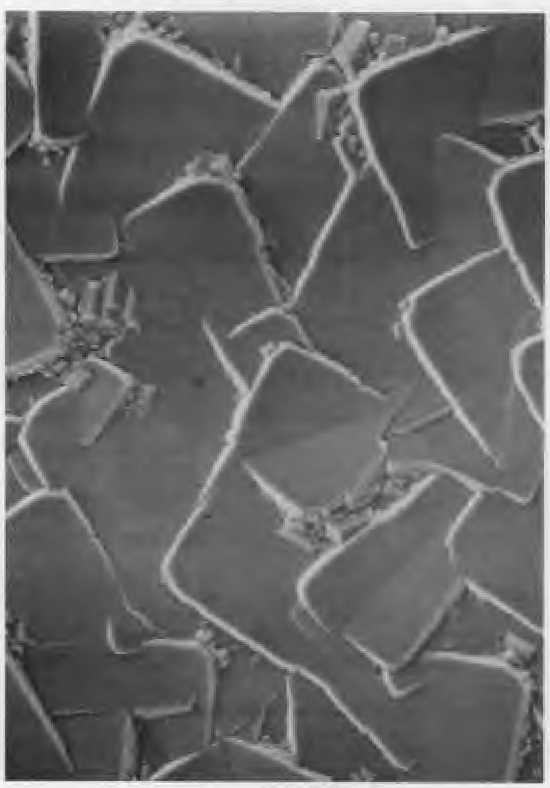
According to recent reports, a completely different method not requiring plasmas or heated substrates is ion implantation. In this approach, carbon ions are accelerated and then rammed into the substrate, creating a local high-pressure environment. Ion implantation produces a diamond film slowly but uniformly, and it can coat a much larger area of substrate than CVD methods.

Clausing explains that he chose the hot-filament CVD method because it has fewer variables and thus is easier to control for the results he wants. He and his colleagues are studying the effects of variations in growth conditions, such as temperature and gas composition, on the properties of the deposited film. Different surface morphologies, ranging from rough to smooth, can be achieved by controlling the growth conditions.

A rough surface, which may be used for abrasives, results from a predominance of octahedral-shaped crystals, which resemble miniature pyramids. The faces of the pyramids are described as {111} because those numbers are the approximate intercepts such a face would have



Polycrystalline diamond films like the one shown in this micrograph may soon be used for abrasives and for surfaces of cutting tools.



Researchers in ORNL's Metals and Ceramics Division study how controlling the growth conditions of a film influences the surface morphology. Here, a scanning electron micrograph of a film dominated by {100} crystal faces shows a smooth surface that may be used in anti-friction applications.

with superimposed x, y, and z axes. On the other hand, a smooth film, which may have good optical, electronic, or antifriction applications, results from the predominance of cube-shaped crystals, whose faces are described as {100}. The reason why one particular shape of crystal determines the texture of the film lies in the early stages of diamond film growth.

"Initially the crystallites are all oriented in a random fashion on the surface," Clausing explains. "Then as the film grows, the ones that are oriented so that their fastest-growing crystal direction is perpendicular to the substrate grow faster. Pretty soon they cover up their neighbors."

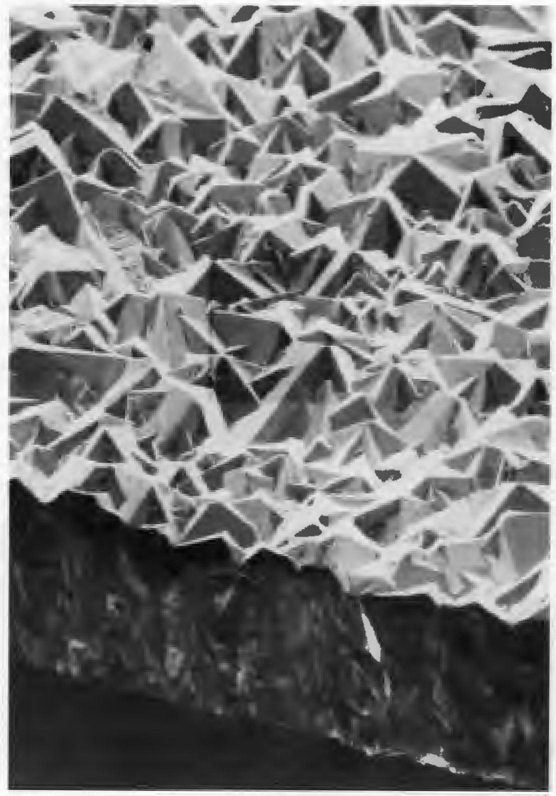
On the surface of a film, only the crystallites that survived are visible. Break the film in half, and a columnar structure appears that reveals the development of the film. By regulating the growth conditions of the film, Clausing and Heatherly can produce the desired texture during a particular experimental run.

"It gives you a tremendous degree of control over the material you grow," he says. "You can choose whether you have pyramids on the surface with four sides or whether you have the same crystal orientation but you have flat surfaces on top. We still don't entirely understand all of the mechanisms."

Uses for Diamond Films

Applications for diamond-coating technologies range from everyday products to futuristic electronics. Currently on the market are a thin window for X-ray instruments and a Sony digital audio speaker with a diamond-enhanced speaker. In the next few years, diamonds will probably be used for superior wear-resistant cutting tools and for abrasive grit. The crystalline films are suited for tools such as drill bits because, if the cutting edge is used so much that it becomes dull, the crystal will break to expose a fresh cutting surface. The rough surfaces are dominated by {111} faces, which contain major microstructural defects such as stacking faults and twins, along which the crystal will tend to break. The tools may last up to ten times longer with a diamond coating. Diamond is extremely strong and hard and may also be used to reduce friction and wear; it has a low coefficient of friction (around 0.1) if grown with a smooth, flat surface.

Future hopes for diamond coatings include diamond electronics and semiconductors. Diamond's natural resistance to radiation, corrosion, and chemical attack make it a highly desirable material. Because it can be made into a semiconductor and is an excellent conductor of heat, it could be used in computer chips in place of silicon; diamond elements could be placed closer together without danger of overheating (they can operate at 600°C), thus increasing computation speeds. However, the polycrystalline diamond films currently being produced cannot be used for electronics. Microstructural defects such as twins, stacking faults, and dislocations provide traps for charge carriers.



A film dominated by {111} faces has been broken in half to reveal the columnar structure created during its early growth, as shown in this micrograph.

Continuous Single-Crystal Diamond Film?

If the dream of electronics is to be realized, a single-crystal continuous diamond film is desirable. Growing such films has become a major challenge for the diamond industry.

Single-crystal diamond films have been grown on natural diamond substrates, but commercialization of the process is prevented by the high cost and limitations imposed by the availability of natural substrates. Recent results from two experiments involving the implantation of carbon ions suggest that it may be possible to grow diamond films on crystalline copper substrates. Copper was chosen as the substrate because its interatomic spacing is very close to that of diamond, making it an effective template for diamond growth. In addition, carbon atoms do not react chemically with copper, and they diffuse to the material's surface at high temperatures.

In one experiment, termed "implanted-atom-out diffusion epitaxy" (reported in September 1990 by J. F. Prins and H. L. Gaigher at the 2nd International Conference on New Diamond Science and Technology), copper substrates at elevated temperatures (about 990°C) were implanted by carbon ions. At these temperatures, the implanted carbon diffuses readily to the surface to form a carbon layer. Evidence of diamond crystallites in this layer was claimed.

In a related experiment reported on in an April 1991 issue of *Science*, J. Narayan and V. P. Godbole, both of North Carolina State University, and C. W. (Woody) White of ORNL's Solid State Division claimed that thin diamond films were formed during pulsed-laser processing of copper substrates implanted with carbon ions. In this experiment, an accelerator at ORNL's Surface Modification and Characterization Research Center was used to implant carbon ions into copper substrates up to a concentration of 10^{18} atoms per square centimeter of copper surface. These substrates were then irradiated with a pulsed laser and characterized at North Carolina State University.

Pulsed-laser irradiation melts the near-surface region of the copper containing implanted carbon atoms. As the liquid layer begins to solidify, the liquid-solid interface moves rapidly toward the surface. The researchers hoped that the carbon

This micrograph made by an atomic force microscope in the Health and Safety Research Division provides quantitative information about the surface topography of a diamond film, which is useful in understanding film growth processes.

atoms would cluster during solidification and form diamond. The formation of thin, continuous diamond films over several square micrometers of copper substrate was claimed.

Diamond film formation by either implanted-atom-out diffusion epitaxy or laser processing of copper substrates implanted by carbon ions is controversial at present because of difficulties in achieving reproducible results. Nevertheless, scientists in the Solid State Division (including Steve Withrow, Woody White, and Ray Zuhr, working with Doyle Hembree of the Oak Ridge Y-12 Plant) continue to explore the possibility of using these methods to produce diamond films over large areas. Much of this research is being carried out in collaboration with scientists from other institutions; including the University of North Carolina, North Carolina State University; Northwestern University; and Forschungs-zentrum, Jülich, Germany.

Other Diamond Film Research

Other researchers at ORNL also study diamond films. Working with Clausing, Horton, and Heatherly are E. D. Specht of the M&C Division, an X-ray diffraction expert who determines the crystal orientation and residual stresses; Karren More of the M&C Division, who did the initial transmission electron micrographs of the films; and Z. L. Wang of the University of Tennessee, an electron microscopist who studies crystal defects in the films. Hal Kimrey and Walt Gardner, both of the Fusion Energy Division, are working with plasmas to demonstrate large-area depositions and to develop diagnostics for controlling the growth environments for diamond films. Mike Ramsey, Bob Shaw, and Bill Whitten, all of the Analytical Chemistry Division, are focusing on laser diagnostics for diamond film analysis. George Begun, who is now retired from the Chemistry Division, used Raman spectroscopy to determine diamond film quality. Jeffrey Glass and Mike Ma, both of North Carolina State University, use the SHaRE Facility at ORNL to study the nucleation and growth of diamond films. In the Health and Safety Research Division, diamond film structure has been studied using an atomic force microscope (see micrograph above). This instrument is being used to obtain quantitative data on surface topography microstructure down to near-atomic dimensions.

Future of Diamond Coatings

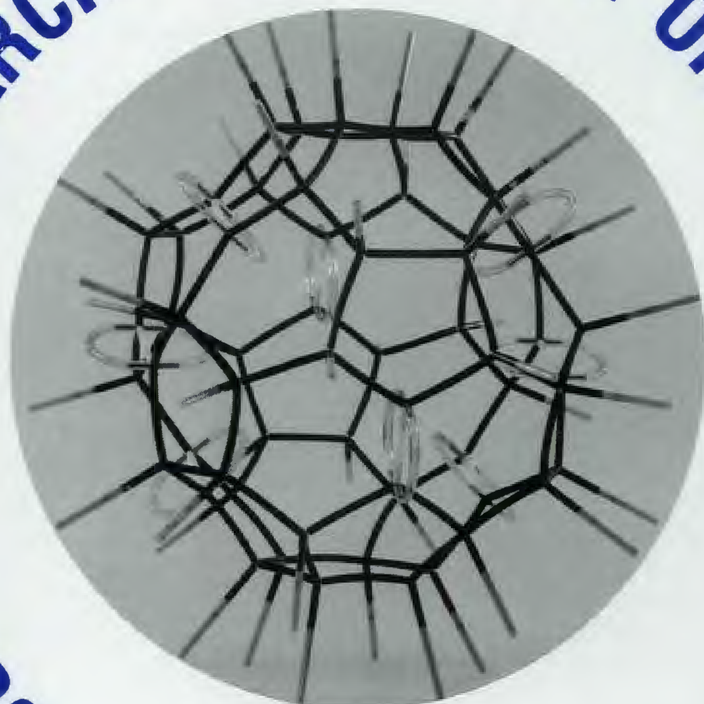
International efforts continue in the field of diamond-coating research. The Russians and the Japanese, who were among the innovators in CVD diamond technology in the late 1970s and the 1980s, remain avid researchers in the field. Since 1984 in the United States, a resurgence of interest in this area has occurred. In 1987 Pennsylvania State University set up a research consortium of more than 27 members, including industry giants such as Raytheon and Texas Instruments, who pay $20,000 annually to share diamond technology. Last summer, Clausing directed the North Atlantic Treaty Organization (NATO) Advanced Study Institute, which

Alexandra Witze, author of this article, worked at ORNL in the summer of 1991 as a science writing intern for *the ORNL Review*. She is a senior at the Massachusetts Institute of Technology, where she is majoring in geology. Here, she discusses an article she wrote for the ORNL monthly newsletter *Lab Notes* with its editor, Bill Cabage.

studied diamond-coating technology and boasted representatives from 17 countries, including the United States, the Soviet Union, Japan, England, Germany, Austria, and Sweden. "The technology," he says, "is rapidly spreading all around the world."

The superlative properties and potential advantages of diamond films ensure further development of the technology. Perhaps one day diamond will become an everyday part of our lives, as our fantasies draw closer to reality. John Angus, one of the pioneers in CVD diamonds, expressed his lifelong dream to Clausing during a visit to ORNL several years ago. Thin diamond films aren't quite satisfying enough, it seems, because Angus told Clausing, "I want a diamond as big as a suitcase."

BUCKYBALL RESEARCH ON A ROLL AT ORNL



The suggested structure for a fluorinated buckyball ($C_{60}F_{44}$) is shown in this model. Fluorinated buckyballs could be used as lubricants.

Until 1985, diamond and graphite were the only two known forms of crystalline carbon. In that year, however, a new class of carbon structures was discovered, the most famous of which are the 60-atom clusters (C_{60}) popularly called "buckyballs." Buckyballs have initiated a flood of research because of their unusual properties, including their potential use in high-temperature superconducting devices.

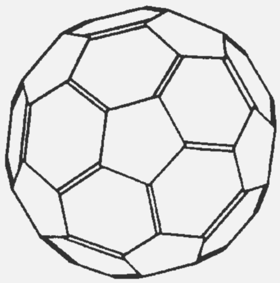
Several ORNL and University of Tennessee (UT) scientists are at the forefront of this exciting new field, which was opened up by the initial discoveries of R.E. Smalley (Rice University) and H. Kroto (University of Sussex, UK). An ad hoc ORNL team studying large carbon clusters includes Bob Compton, Eph Klots, and Rufus Ritchie, all of the Health and Safety Research Division; Bob Hettich of the Analytical Chemistry Division; and Dave Geohegan of the Solid State Division. This group is joined by Don Armstrong and Dave Harkins, both of the Oak Ridge Gaseous Diffusion Plant, and Jim Adcock and Al Tuinman, both of the University of Tennessee.

Carbon clusters, composed of from 28 to over 540 carbon atoms, belong to a class known as "fullerenes." A buckyball is an especially stable fullerene containing 60 carbon atoms in the shape of a soccer ball. "It's been called soccerene in America and footballene in Europe," says Compton. Technically the molecule is described as a truncated icosahedron because it has 12 pentagonal faces and 20 hexagonal faces. It was named buckminsterfullerene because it resembles the geodesic dome favored by the architect R. Buckminster Fuller—hence the nickname "buckyball."

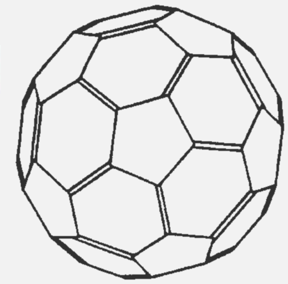
The explosion in buckyball research was prompted by recent discoveries of ways to make gram quantities of C_{60}. The molecule had previously been produced only in microscopic quantities, but in mid-1990 physicists in Germany and at the University of Arizona found that they could use an arc welder to vaporize graphite rods in helium gas to produce a magical "soot." The soot contains up to 40% C_{60} and C_{70} as well as other fullerenes, which can be extracted into hot benzene to create a wine-red solution and then isolated by evaporating the liquid.

Another method of synthesizing C_{60} is laser ablation in a helium atmosphere—shining laser light on graphite to create a plasma of hot atoms and ionized gas, from which fullerenes can grow. "ORNL is doing a considerable amount of laser ablation research, ranging from producing high-temperature superconducting films to C_{60} molecules," says Compton. In April 1991 the Laboratory hosted an international conference on laser ablation applications that drew experts from around the world.

"Laser ablation isn't used much anymore to make buckyballs unless you want to dope them," explains Compton. "You can use graphite laced with dopants (impurities added to a pure substance) so that the dopant atoms become trapped inside or outside the cage of the



"ORNL researchers have observed that buckyballs can take on additional electrons, suggesting that they could be used for batteries and superconductors."

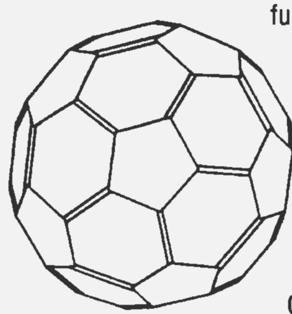


buckyballs." Certain dopants turn buckyballs into organic superconductors and other useful materials. Laser ablation, however, remains the method of choice for producing new "magic number" clusters as well as modified fullerenes.

"The really hot topic right now involving dopants," says Compton, "is placing alkali and other atoms around the C_{60} cage to create high-temperature molecular superconductors." Scientists at Allied-Signal, Inc., have made a rubidium-thallium-buckyball superconductor that works at 42 K.

Potential applications for fullerenes include not only superconducting devices but also high-temperature lubricants, because the spherical molecules roll against each other and on surfaces easily. Blau and his colleagues are actively studying the frictional properties of buckyballs. Construction of lightweight batteries using carbon clusters is also under consideration. It is thought that fullerenes may also be useful as catalysts or more efficient semiconductor chips, and they may be used to make rocket fuel and encapsulate radioactive atoms for detecting and treating cancer.

Someday buckyballs may help astronomers explain the origin of the universe. The first hint that buckyballs might exist came from astrophysicists who attributed unusual spectral lines to a then-unknown molecule such as C_{60}. It is now believed that C_{60} molecules exist in outer space primarily in the ionized form. It has been suggested that if buckyballs are present in large quantities in interstellar space, they may well be the substance around which all matter accreted.



"Much of the work we've done here at ORNL is unique," says Compton. He has filed for a patent on a method for separating fullerenes from graphitic soot while simultaneously separating the different fullerenes from one another.

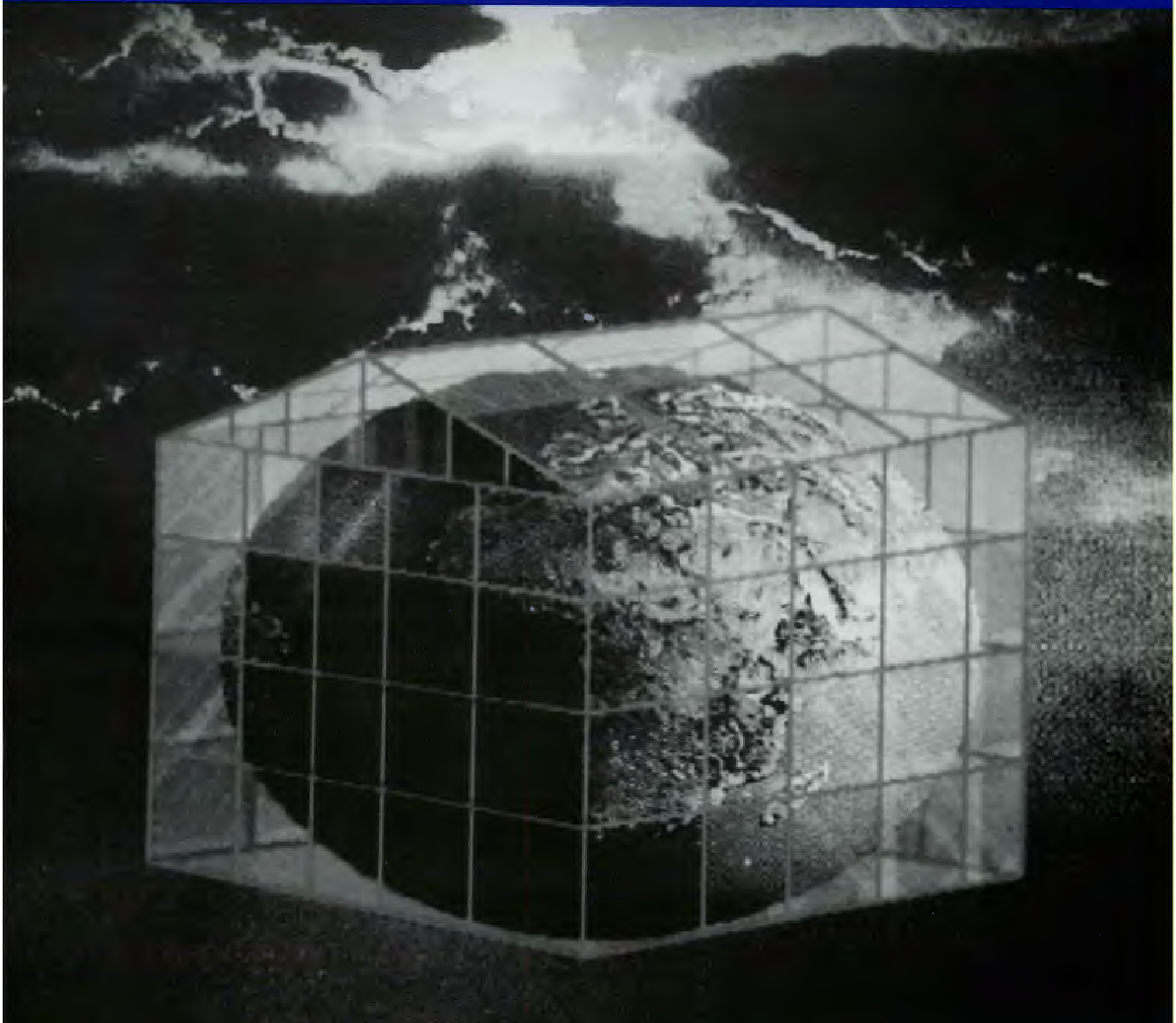
Hettich, Compton, and Ritchie have observed that, in the gas phase, C_{60} and C_{70} can take on two additional electrons, resulting in doubly charged negative ions. "This unusual behavior," says Compton, "suggests that C_{60} could be used for long-lived, lightweight batteries and superconductors."

Klots has observed that C_{60} evaporates at an uncommonly slow rate when energy is added, resulting in the "boiling off" of electrons, not whole atoms. This unexpected behavior further supports the idea that C_{60} could be a high-temperature superconductor. Mike Guerin of the Analytical Chemistry Division has begun to coordinate health studies on the effects of buckyballs on humans. "We have to be careful with any new material we discover," warns Compton. Graphitic soot has caused cancer in chimney sweeps for centuries; the disease is probably not caused by fullerenes, but this hypothesis must be tested.

Other researchers associated with ORNL are aiding in the study of the unusual properties of fullerenes. A visiting scientist from the former Soviet Union, Alex Puretzky, is studying doped C_{60} molecules for super-conductivity, and Bill Frey of Davidson College, on sabbatical at ORNL in 1991, worked on the synthesis and characterization of buckyballs and higher fullerenes.

Geohegan and Puretzky are trying to understand the growth of carbon clusters from laser ablation; such studies are important in understanding how to produce them more efficiently and to produce higher fullerenes as well as other magic-number clusters. In the Solid State Division, Ted Kaplan and Mark Mostoller are using molecular dynamics calculations to investigate the stability of buckyballs and their interactions with matter. Finally, ORNL collaborations with Adcock and Tuinmann, both of UT's Department of Chemistry, have produced fluorinated buckyballs. They have achieved degrees of fluorination ranging from $C_{60}F_{44}$ (see suggested structure in the figure at left) to $C_{60}F_{48}$. The result of this work could be a highly stable buckyball-based lubricant.—*Alexandra Witze*

Energy Strategies for a Greenhouse Future



Replacing worldwide fossil fuel combustion with nuclear, biomass, and improved efficiency technologies to reduce atmospheric CO_2 concentrations will not be easy.

In June, 1991, Oak Ridge National Laboratory hosted a three-day international conference, Technologies for a Greenhouse-Constrained Society. The conference drew over 200 attendees from around the world to discuss alternative technologies for reducing fossil fuel use over the next few decades. Many of the speakers were ORNL scientists and managers.

The basic assumption of the conference was that all nations must shift their energy emphasis from fossil fuels to clean, efficient, and renewable sources of energy. Fossil fuels are limited resources, but, more importantly, they also contribute significantly to the amount of carbon dioxide (CO_2) in the earth's atmosphere. CO_2 is the primary greenhouse gas that allows sunlight to strike our planet's surface but traps the outgoing infrared radiation inside the atmosphere. According to Stephen Schneider of the National Center for Atmospheric Research, increased CO_2 levels caused by human activity are trapping an extra 2 W/m^2 of energy on the earth's surface. Many scientists believe that this greenhouse phenomenon will cause a gradual global warming and that the altered climate will have marked environmental and socioeconomic impacts.

The ORNL conference focused on three technologies that would help reduce the amount of CO_2 and other greenhouse gases in the atmosphere: nuclear power, biomass, and energy conservation. These technologies were emphasized because they have great potential and are controversial; other strategies include sequestering carbon in trees and using solar or hydroelectric power.

Why should the world begin now to reduce its greenhouse gas emissions? The world's population is expected to reach 12 billion, 2.5 times what it is today, by the year 2100; five years ago, the same projection was 8.5 to 10 billion. As the number of people rapidly increases, the greenhouse problem is automatically amplified because of the increased demand for energy and food. Energy services contribute approximately two-thirds of greenhouse gas emissions; agriculture, most of the remaining one-third. "It is time to get serious," said Robert Socolow of Princeton University.

Stephen Schneider

"Developing nations will have an increasing impact on global climate."

Alex Zucker

Alex Zucker, associate director for Nuclear Technologies at ORNL and chairman of the conference organizing committee, said in his opening remarks that, although some uncertainties still exist concerning the consequences of increasing greenhouse gas levels in the atmosphere, it is a "prudent course" to regard the accumulation of greenhouse gases as significant. An increase in global temperature of 1/2°C has already been observed, and it may rise 2 to 3°C, in the most optimistic predictions, or as much as 5°C.

Zucker noted that analysis of climate change and prediction of socioeconomic and environmental consequences are difficult because of the complex and global nature of the problem. It is a problem that has no precedent, he said, adding that it will require long-term international cooperation and changes in the values by which people live.

Zucker emphasized the need for developing countries to use alternative technologies. This theme became central to the conference, because developing nations will have an increasing impact on global climate. In China and India, for example, CO_2 emissions are rapidly increasing because of heavy coal use and rapid growth. The industrialized nations may be able to level off or even decrease their emissions, but the developing countries, without the energy technologies to replace fossil-fuel combustion, will become major contributors to atmospheric concentrations of greenhouse gases.

The greenhouse problem challenges the notion of exponential development, said John Gibbons, director of the Office of Technology Assessment (OTA) of the U.S. Congress. In the past, exploitation of resources in the name of growth was accepted and popular. Only recently have governments changed their attitudes and attempted to protect public resources, or the commons, for the future. The issue of global warming is the largest commons of all.

Because the United States accounts for a fourth of total global greenhouse gas emissions and because we are highly sophisticated and capable in technology, we carry a heavy responsibility (and opportunity) to lead efforts to reduce greenhouse gases. To be successful, such efforts must be sustained over many decades, said Gibbons, a former ORNL physicist who initiated energy conservation research at the Laboratory.

Gibbons pointed out that greenhouse gas emissions are linked to the ways that people convert resources (such as energy and agriculture) into consumer products and services, as well as to population size and standard of living. Technology can be used to reduce greenhouse gases and still produce goods and services.

OTA studies, confirmed by a recent report from the National Academy of Sciences, show that technology can achieve both goals, if encouraged by public policies. Without such efforts, U.S. CO_2 emissions will increase by 50% (by 2015 compared to 1987); with modest and cost-effective steps, the increase could be held to 15%; and with vigorous but sensible measures using known technology, emissions could actually be cut by 30%. Gibbons said that such leadership efforts are needed to spur the developing world to take similar steps.

John Gibbons

Can we cut our dependence on fossil fuels? asked William Fulkerson, associate director for Advanced Energy Systems at ORNL, who was a replacement speaker for DOE's Assistant Secretary for Conservation and Renewable Energy, Michael Davis. The world is dependent on coal, oil, and gas for 75% of its energy, Fulkerson said, adding that this dependence must be cut in half to stabilize CO_2 levels. He noted that the United States must reduce its dependence on fossil fuels by over 90% if every person on the globe is allotted the same emission rate. Such drastic reductions may seem unachievable, he said, but they are possible.

Our dependence on fossil fuels could be significantly reduced, Fulkerson said, if the United States were to make much greater use of energy efficiency; nuclear power; renewable sources of energy such as biomass, hydro, and solar power; and carbon sequestration. Only by combining greatly improved efficiency with greatly expanded use of renewable and nuclear energy sources can the United States possibly achieve a 90% reduction of CO_2 emissions in 50 years.

"To make the cost reasonable," Fulkerson said, "much better technologies are needed, and a significant increase in research, development, and demonstration investment is warranted. Additionally, the choices made by developing nations will be crucial, and the industrialized world should devote considerable resources to providing better technological and institutional choices."

"We carry a heavy responsibility (and opportunity) to lead efforts to reduce greenhouse gases."

Nuclear Energy

Alvin Weinberg, former ORNL director, introduced the initial session on nuclear technology with a history of nuclear power. He described the development of nuclear reactors from the historic moment in December 1942 when the first chain reaction was observed by Enrico Fermi's team in Chicago to the present when more than 400 reactors are operating. ORNL has continually played a large role throughout this history.

However, Weinberg said, the future of nuclear power is uncertain. There will be a second nuclear era only if public perception of the technology changes. People fear the production of radioactive waste, meltdown accidents, and the possible diversion of reactor-produced plutonium to military uses. According to Weinberg, Fermi foresaw at the dawn of the nuclear age that the public would dislike the growing amounts of radioactive waste produced by reactors. The accidents at Three Mile Island and Chernobyl, he added, have only increased the public's fear of nuclear energy.

Robert Uhrig, an ORNL–University of Tennessee Distinguished Scientist, told some "success" stories that suggested a second nuclear era is possible. Entitled "Enabling Technologies:

Alvin Weinberg

How Do We Get There?" his talk included a description of the success of Electricité de France (EDF) in establishing nuclear power as a major energy source. Using U.S. technology, EDF built a group of reactors between 1977 and 1984 that are operating safely and efficiently, providing 65% of France's electricity. By contrast, in 1990, the United States had 111 operating nuclear power plants, providing 21% of its electricity; 57% comes from coal-fired plants, 12% from oil and gas, and 9% from hydroelectric facilities.

Uhrig also told the history of the St. Lucie reactor in Florida, which was constructed quickly and efficently by the Florida Power and Light Company. Many quality checks have been made to ensure the safety of the reactor, he said. When Hurricane David passed through the area in 1979, he noted, the construction program was disrupted, but within a year the program was back on track.

Uhrig argued that a second generation of nuclear power plants is needed. Because electricity consumption is growing in the United States at the rate of 2.5 to 3% every year, said Uhrig, large numbers of plants need to be built. It is estimated that 4000 to 5000 nuclear reactors operating in the world would make nuclear power the primary energy source.

Concerning nuclear energy, Fulkerson said, "To achieve public acceptance, international cooperation will be needed. In the current climate, a nuclear accident anywhere in the world is an accident everywhere. Stronger international controls are needed to deal with the proliferation issue; Iraq is a vivid example. Finally, cooperative research and development and universal standards could help promote public acceptance of nuclear power."

Biomass

According to Fulkerson, a recent study has concluded that the potential contribution of renewable energy technologies to the U. S. energy supply could grow from the current 6.8 quads of primary energy equivalent to about 41.6 quads by the year 2030. About half of this total, he added, is assumed to come from biomass sources.

Another option for dealing with the greenhouse effect, Fulkerson noted, is to sequester CO_2 in biomass. "Sequestering CO_2 in biomass," he said, "includes both using biomass fuels to displace fossil fuels, with the result that carbon emissions are recycled through the fuel with no net increase to the atmosphere, and reforestation to offset fossil emissions.

"Cost estimates for sequestering CO_2 in biomass range from –70 to +40 dollars per ton of carbon. The negative $70/T of carbon assumes that biomass can be grown on plantations at $2/GJ and that the fuel is used to produce electricity by gasification and advanced gas turbines. If this technology were to replace conventional coal-based Rankine cycle conversion, the biomass system would actually be cheaper and produce no net CO_2 in the atmosphere."

CO_2 emissions would level off from 2010 through 2030 if biomass fuels are used in place of coal, oil, and natural gas. According to Jack Ranney of ORNL's Environmental Sciences

William Fulkerson

Robert Uhrig

Jack Ranney

Division, the full-scale use of ethanol and other fuels produced from biomass crops in that time could avoid the generation of one billion tons of CO_2 from fossil fuels.

Ranney said this estimate is conservative compared with estimates of others because he believes that the use of biomass for fuels will be limited by several factors. He listed government restrictions on clearcutting, limitations on the use of land for biomass crops because of its poor quality, and the biodiversity issue—especially concerns about endangered species.

Conservation

Improving energy efficiency is much less difficult than reducing the costs and risks associated with other options, said Eric Hirst, a corporate fellow in ORNL's Energy Division. Nuclear waste, oil spills, deforestation, and other problems can be avoided if those responsible for energy efficiency—the government, utilities, manufacturers—work together to implement energy-saving measures. Institutional barriers to energy efficiency must be removed before behavioral, or personal, barriers can be lifted. According to Hirst, the benefits of energy efficiency, besides reduced CO_2 emissions, include a healthy economy, increased U.S. competitiveness in foreign markets, environmental quality, and national security.

Because market forces alone cannot bring about efficiency, Hirst said, the government and utilities must both play large roles. The Department of Energy, he added, should expand research and development programs to concentrate on improvements such as windows designed to cut energy losses by 90%. A few changes like this may make conservation attractive and viable.

Hirst also noted that, because more than half of the U.S. energy budget passes through electric and gas utilities, they should be encouraged to run conservation programs. As an example, Hirst said, if the Tennessee Valley Authority made energy-efficient, compact fluorescent bulbs available, the public would buy the light bulbs, thus removing a key institutional barrier (lack of local availability of these lamps). Many private utilities around the nation are already providing this service.

To protect the environment and national treasuries, energy efficiency improvements should be implemented globally, an ORNL Corporate Fellow told the conferees. Thomas Wilbanks of the Energy Division argued that

Eric Hirst

Thomas Wilbanks

energy efficiency improvements in industrialized nations and the 70 developing nations would significantly reduce both CO_2 emissions and capital expenditures for energy services. Energy efficiency improvements aim to reduce the energy use of buildings and appliances, transportation vehicles, and industrial processes.

The demand for energy services in developing nations will continue to grow and will be met largely by coal and oil combustion, Wilbanks predicted. Because of fears about the possibility of global warming, he said that these countries will be pressured to reduce their dependence on coal and oil and to substitute natural gas and biomass fuels.

Alternatives such as nuclear power, hydro-electric dams, and solar electricity will probably not be pursued in these countries, said Wilbanks, because of the large capital requirements. He pointed out that the capital costs for energy service expansions in the 70 countries could total $100 billion a year, a daunting amount considering that the total indebtedness for these nations is already a trillion dollars.

Developing countries must meet their energy needs, Wilbanks said, adding that failure to do so could result in equipment damage, product spoilage, and political turmoil. The most cost-effective way to provide adequate energy services is to implement energy-efficiency improvements.

Wilbanks said that energy-efficiency improvements will more likely be deployed in developing countries if the U.S. government and utilities take a lead in implementing them in the United States.

Over the next 20 years, efficiency improvements are expected to reduce the growth of energy use in the United States by 12%, said Roger Carlsmith, director of ORNL's Conservation and Renewable Energy Programs. An additional 13% gain in efficiency would be cost effective but is unlikely to occur unless the government provides stronger incentives to overcome barriers.

In many cases, Carlsmith said, consumers make logical decisions that benefit them as individuals but not necessarily the nation as a whole. From a national perspective, he noted, the benefits of energy-efficiency improvements would be energy security, increased competitiveness in international commerce, and reduced global warming.

International Efforts

The third and final day of the conference was devoted to international speakers describing the situations in their native regions. The message was clear: Developing countries are finding it difficult to replace fossil fuel use with alternative energy technologies, mostly because of a lack of experts and modern equipment.

For example, a country might have a newly built nuclear reactor but be unable to operate it because no one knows the safety procedures. There may be a ten-year lag in technology flow from the United States and other industrialized countries to the developing ones.

Nevertheless, CO_2 emissions from countries such as China, India, and Mexico are an increasing part of total global emissions each year. The consensus of the conference was that these countries and others must find ways to control emission levels.

Arun Kumar from Development Alternatives in India suggested that, for his country, biomass fuel is the most practical alternative to coal and oil. Biomass is readily available in India, and it can be used as fuel by residents without greatly disturbing their traditional way of life, especially in rural areas.

Energy efficiency might be the best choice for some of these countries, but it is difficult to implement because of poor planning and an unwillingness to share responsibility, said K. V. Ramani of the Asian and Pacific Development Centre. Many people just "don't understand the crisis," he said. Alternative technologies for underindustrialized nations may take quite some time to implement.

Summary

Socolow of Princeton University summarized the results of the conference by saying that a likely subtitle for the meeting might have been "misery loves company," because nuclear, conservation, and biomass technologies are not taken seriously outside of a limited number of advocates. However, he noted, the Oak Ridge conference directly addressed the problems of each technology.

Challenges to nuclear power include overcoming the public's "nuclear fear" and bringing more young scientists and engineers into the field. Socolow called for the dissociation of the "military atom" from the "civilian atom" by asking executives at nuclear power utilities to promote worldwide disarmament. Until the public is convinced that nuclear power is safe, he said, its advancement will be severely limited. Others disagreed with the call for disarmament, saying that nuclear power executives had too many other problems to worry about.

Socolow described the biomass alternative as being at the resource assessment stage, just as uranium was 30 years ago. The greatest challenge facing the use of biomass is the issue of land use. Socolow noted that the growth of biomass crops should be thought of as restoring degraded land and not as invading pristine wilderness. If the environmental movement decides politically to support the use of biomass, this energy source may advance more rapidly toward practical applications. The prospects seem good for liquid fuels from biomass crops.

Roger Carlsmith

Proponents of energy conservation have begun to realize its limitations, said Socolow. Energy efficiency faces a gap between available technology and full-scale use. Once a social service, today it has become a necessary means of reducing consumption. By 2010, cars may have a gasoline-use efficiency of 55 miles per gallon, but increased travel will undermine the gains in efficiency. Socolow concluded that more effort is needed to demonstrate the advantages of conservation.

—Alexandra Witze, summer student intern who is now a senior majoring in geology at the Massachusetts Institute of Technology.

Sensors for Health and Safety

By Carolyn Krause

A drunken intruder staggers into a house, setting off a burglar alarm. Panicking, he runs through the house and trips over a space heater, knocking it down on a pile of newspapers. The paper begins to smolder, and as the intruder struggles to his feet, he hears the loud buzz of a smoke detector. He bolts from the house and speeds off in his car. Five minutes later, he hears a police car siren and stops only to learn that he has been caught in a radar speed trap. The police officer asks him to blow into a breath tester and then arrests him for driving under the influence of alcohol.

Burglar alarms, smoke detectors, radar speed traps, and breath testers are common examples of sensor technology developed to protect public safety. Sensors and detectors are devices used to detect the presence of something. Some sensors, such as the breath tester, not only detect the presence of something but also measure its concentration.

Some of these instruments may also be used for research, environmental monitoring, and process controls. They are being developed by the Instrumentation and Controls (I&C) Division in conjunction with other ORNL organizations, such as the Environmental Sciences Division and the Metals and Ceramics Division. They include radiological, radiofrequency, optical, and chemical detectors. Most of these sensors have been (or are expected to be) awarded prizes, patented, or licensed to industrial firms.

Radiological Detectors

Alpha/beta/gamma field survey instrument. At the Oak Ridge K-25 Site and the Y-12 Plant, hundreds of face masks that are used to protect workers from toxic airborne substances must be cleaned each day. Then these respirator masks are checked with different instruments for different kinds of radioactive contamination to determine if they can be safely reused—a time- consuming task.

Meanwhile, at ORNL, a technician works half-time to replace the fragile windows of survey instruments used to monitor the environment for alpha radiation; these instruments, like the ones used on face masks, are frequently used to check items in the plant to determine if they should have a "green tag" (allowing them to be safely disposed of in a nearby landfill or reused elsewhere).

Fortunately, however, researchers in ORNL's I&C Division have devised a technique for detecting different types of radiation that is more rugged and efficient than conventional alpha-radiation survey detectors. This invention also could make it easier to inspect respirator masks for radioactive contamination.

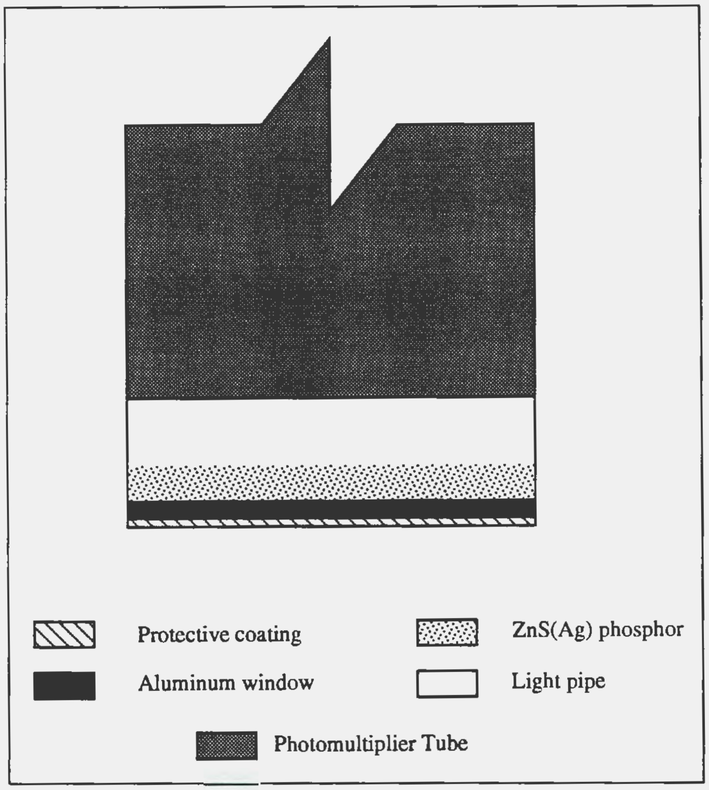
Using funding from the U. S. Navy, I&C researchers have developed a rugged alpha detector that has the potential to revolutionize health physics instrumentation. Martin Marietta Energy Systems, Inc., has licensed the new alpha sensor technology to the Dosimeter Corporation of Cincinnati, Ohio, for development of a complete alpha field-survey instrument. The ORNL researchers also have developed a concept for incorporating alpha, beta, and gamma detectors in one sensor, which could reduce the labor required for surveying gas masks and other items for several types of radioactive contamination.

The new detector was developed by Stephanie McElhaney, Jim Ramsey, Martin Bauer, and Marion Chiles. The key to making it more rugged and efficient, said I&C group leader Bauer, has been replacing the fragile Mylar window with an "embedded scintillator powder in a plastic light pipe."

Mylar windows on alpha detectors are constantly breaking and must be replaced. These thin aluminized plastic films can be easily harmed by corrosive chemicals and punctured; scratched; or

At ORNL, four types of sensors have been or are being developed primarily for protecting human health and safety.

Stephanie McElhaney displays a new scintillation detector designed primarily for field surveying or personnel monitoring of alpha contamination. The new unit developed at ORNL is more compact and uses a special surface treatment to resist physical damage and attack by chemicals. The older model is shown lying on its side.



Schematic of the rugged ZEALS detector developed at ORNL.

torn easily by gravel, sand, and screwheads present during environmental monitoring of wastewater streams and weapon test sites. Like ORNL, the U. S. armed forces find it impossible to keep these fragile alpha instruments in the field for surveys of soil, sticks, vehicles, and other items, so they are searching for alternatives.

A rugged field survey instrument that can detect alpha, beta, and gamma radiation, says Bauer, could be used to monitor respirator masks at the Oak Ridge K-25 Site for contamination by radioactive materials such as uranium dust. All masks must be cleaned at the end of each day to make them sanitary and free of contamination. Before they can be reissued, the masks must be inspected for alpha, beta, and gamma radiation by two or three different instruments to ensure that they are free of contamination. According to Bauer, use of one instrument molded to the shape of a mask and able to detect all types of radiation could save considerable time and cut labor costs.

A conventional alpha survey instrument consists of a "scintillator" attached to a photomultiplier tube housed in a light-tight instrument. A scintillator emits light in the presence of ionizing radiation, and the light intensity indicates radiation levels. The scintillator used conventionally is a plastic light pipe covered with a phosphor of silver-activated zinc sulfide. The emitted light is detected and amplified by a photomultiplier tube, which converts it to an electric signal. The actual alpha particle count is displayed on a monitor.

"The problem with alpha particles," says Bauer, "is that they have very low penetrating power." Thus, the entrance window in front of the scintillator must be very thin so that the alpha particles will pass through. In addition, because the photomultiplier tube must detect only light emitted by the scintillator, the entrance window must keep out ambient light. A popular light-shielding material is aluminized Mylar—a very thin plastic film that lets alpha particles through and carries a thin film of aluminum to exclude ambient light. Of course, if the Mylar window is torn or punctured, ambient light will invade the detector and render it useless.

In an effort to combine improved efficiency and ruggedness in a single alpha survey detector, ORNL researchers have developed a more rugged alpha detector. It replaces the fragile Mylar window with a thin, evaporated layer of aluminum protected with a thin hardcoat. The scintillator consists of scintillating powder embedded in a plastic light pipe (which carries light from the irradiated powder to the photomultiplier tube). In this innovation, the scintillating powder, usually silver-activated zinc sulfide, is mixed with transparent epoxy and allowed to settle to the bottom of the epoxy after it is poured into a mold. The smooth scintillator that forms can be covered with a thin scuff-resistant aluminum coating that excludes ambient light. Because the new detector uses zinc sulfide/epoxy alpha scintillation, it is called a ZEALS detector.

Tests have shown the ZEALS detector to be strong, durable, and slightly more efficient than conventional alpha scintillation detectors. An instrument incorporating alpha, beta, and gamma sensors can be made when the optically transparent epoxy binder of the alpha detector is replaced with a special plastic that is beta sensitive. The alpha and beta interactions within the new medium are distinguished by the degree of decrease in light intensity over time (decay constants) of the scintillating materials for alpha and beta particles. A scintillating material with yet another response time can be incorporated behind the settled scintillator to detect gamma radiation.

An ORNL physicist displays a new, compact detector developed at ORNL by combining lithium-6 glass and BC-501 liquid scintillators. This unit is capable of discriminating among slow neutrons, fast neutrons, and gamma radiation.

"Detection and measurement of neutron radiation is particularly important in nuclear facilities and weapons storage areas."

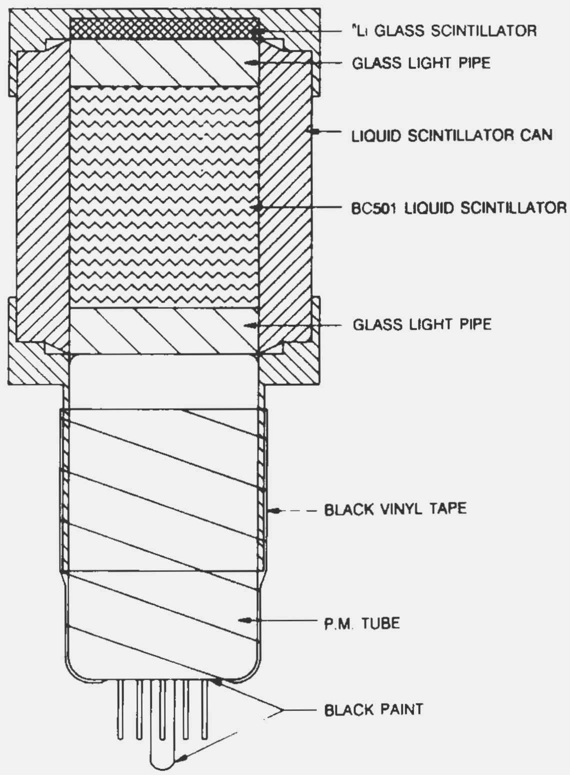
Radiation detector for groundwater. In 1990 an ORNL-developed submersible device for detecting radioactivity in groundwater and shallow surface water was licensed by Martin Marietta Energy Systems, Inc., to Sorrento Electronics of San Diego, California. The in situ Cerenkov radiation detector was developed for field surveillance of groundwater by I. Lauren Larsen of the Environmental Sciences Division and Marion M. Chiles and Clint Miller, both of the I&C Division. The radiation detector detects and measures the concentrations of beta-emitting radionuclides, such as strontium-90, in groundwater by measuring the blue Cerenkov radiation from the high-energy beta particles as they pass through the water sample.

Multi-energy neutron detector. Detection and measurement of neutron radiation is particularly important in nuclear facilities and weapons storage areas. A higher than normal level of neutrons could indicate runaway fission and the potential for a release of hazardous amounts of radioactivity.

Neutron radiation is conventionally measured by a detector consisting of a neutron-sensitive proportional counter inside an 11.4-kg (25-lb) polyethylene ball, which slows down high-energy neutrons so they become thermal neutrons. This device, known as "Snoopy," is unwieldy and difficult to carry.

Chiles, Bauer, and McElhaney have taken a concept developed by John Mihalczo, also of the I&C Division, and expanded it for use as a lightweight multi-energy neutron detector for separately counting thermal neutrons, high-energy neutrons, and gamma rays. Mihalczo had previously demonstrated that the ORNL neutron detector could be used to measure gamma radiation and both fast and slow neutrons in subcriticality measurements on nuclear fuel.

According to Bauer, if funding is made available, the I&C Division would like to further develop this neutron detector for personnel



Schematic of the dual-scintillator neutron detector.

dosimetry because it is more compact and portable and more sensitive to varying neutron energies than conventional neutron detectors. Thus, it could be particularly useful in measuring neutron exposures.

The ORNL detector consists of two scintillators: (1) a glass loaded with lithium-6 that efficiently captures slow neutrons and emits light and (2) a liquid scintillator that produces light by proton recoil following bombardment by fast neutrons. Differences in the amount of reduction of the intensity (decay time) of the light generated by the scintillators permit separate measurements of slow neutrons, fast neutrons, and gamma radiation.

Radiofrequency Dosimeter

The public is concerned about the health effects of electromagnetic fields emanating from transmission power lines, video display terminals, household appliances, and electric blankets. Electromagnetic field radiation is thought to be linked to cancer and birth defects. However, the potential hazard to the general public, says Bauer, is not nearly as great as the hazard to technicians who repair radar devices and radio communication equipment. These mechanics could be subjected to electromagnetic radiation of higher frequencies and field strengths.

The U.S. Navy has sought a device to measure the cumulative dose of this nonionizing radiation to shipboard personnel, who are exposed to electromagnetic radiation from radar and communication systems. The goal is to determine whether a crew member working in a certain area of a ship or aircraft carrier is at risk of exposure to levels above the existing acceptable limit.

"Today's standards for electromagnetic radiation exposure are based on the thermal effects of electromagnetic radiation on the human body," said Dick Hess, a group leader in the I&C Division. "The permissible levels have been set by the American National Standards Institute."

To determine whether individuals aboard ship should be moved to a different work location to reduce exposures to electromagnetic radiation, a personal radiofrequency (rf) dosimeter has been developed for the Navy by Hess, Barbara Hoffheins, Mike Moore, Bob Rochelle, Paul Ewing, and Bob Thomas, all of the I&C Division. The rf dosimeter can be used in the same way as a personal radiation dosimeter, which indicates whether a worker in a nuclear facility is being exposed to excessive radiation and should be relocated to another work site.

The rf dosimeter readings, Hess says, may eventually be helpful in establishing possible links between high-frequency electromagnetic radiation and harmful health effects. It is, however, too early

Michael R. Moore sets up test equipment to measure the sensitivity of a radiofrequency dosimeter developed at ORNL. This pocket-size cumulative-dose recording device is designed to detect and record for a six-month period the strengths and durations of electromagnetic fields present in work areas.

to draw any conclusions because these effects would be long term.

Currently, ten ORNL rf dosimeters are in use by the Navy for technical evaluation. With the successful outcome of this first phase, the technology will be transferred to industry for production.

The ORNL rf dosimeter is a portable, pocket-size device designed to record the cumulative dose of electromagnetic fields to crew members on Navy vessels. It detects and records the strengths and durations of electric fields present in work areas. Readings are acquired and averaged over a 6-minute period, and values are stored for up to 6 months.

"Currently, ten ORNL rf dosimeters are in use by the Navy for technical evaluation.

The rf dosimeter has a miniature antenna that picks up electromagnetic field signals in a frequency range of 30 MHz to 10 GHz. The diode in the device converts each signal to a direct-current (dc) voltage, and an analog-to-digital converter changes the dc signals into digital information that is compressed and stored by a single-chip computer. The data are downloaded to a personal computer at a later time for display and analysis. Measures of field strength are given as volts per meter and milliwatts per square centimeter.

"Data from our rf dosimeters will be used to determine the variations in the strength of the ambient electromagnetic fields for shipboard personnel over time," says Hess. "In general, these rf dosimeters should increase knowledge of the levels of high-frequency electric fields to which individuals are exposed."

Optical Sensor

In December 1986 at the Surry nuclear power plant in Virginia, hot steam suddenly escaped from a pipe weakened by erosion, killing four persons standing nearby. The cause of the pipe erosion was believed to be the formation of abrasive water droplets in high-pressure steam. For safety reasons, the nuclear industry suddenly became interested in better understanding the properties of "wet steam."

In response to the new interest in characterizing droplets in wet steam, Marc Simpson of the I&C Division developed an optical sensor using two beams of laser light. In this system, a light beam from an argon ion laser is split into two beams and brought back together at an angle to form an interference pattern in space. Water droplets are viewed in this pattern. The spacing between fringes in the pattern allows calculation of the speed of the droplet, and the changing amount of light in the pattern as the droplet moves through it indicates droplet size. Typical sizes of droplets in liquid steam range from 0.3 μm to 5 μm.

Simpson's two-color optical system, however, is not being used to assess the safety of steam pipes in reactors; instead, power plant managers are relying on computer models to predict when steam pipes are likely to fail. Currently, Simpson's innovation is being developed as a process monitor at the Gorgas Steam Plant in Parrish, Alabama, which is operated by Alabama Power Company. There the plant managers are concerned about preventing energy losses that reduce the efficiency of the low-pressure turbine in producing electricity and monitoring the turbine performance to predict when maintenance is needed. One indication of energy loss in high-temperature steam is the formation of a liquid phase as a result of condensation.

"Measurement of the concentration of the liquid phase is a good indicator of the performance of the steam system," says Simpson. "It also allows the plant managers to evaluate whether changes in operation are reducing the cost of the energy input at steam facilities."

Simpson is developing a new two-color visibility measurement in the backscatter mode in a collaborative effort with a group at Tennessee Technological University and the Gorgas Steam Plant. He says that this optical monitor for measuring wet steam may have other particle-sensing applications such as characterizing rocket exhaust particles and environmental particulates.

Chemical Sensors

Problem 1: Although oil spills in the ocean receive the most news coverage, fuels leaking from underground tanks pose a more immediate threat to public health because they contaminate soil and groundwater. The first requirements for remediating a contaminated site are to identify the leaking substance and locate its source.

Problem 2: Safety regulations require that aviation fuels be properly stored and identified to prevent misfueling of aircraft. Technology is needed, for example, to determine whether a fuel has the ingredients for preventing ice in planes flown for long distances at high altitudes. Without deicer in its fuel, an aircraft's fuel lines might freeze, possibly leading to engine failure.

Problem 3: Economists argue that the pricing of each motor fuel should be based on its energy content and other qualities such as octane rating. Technology is needed to rapidly determine a fuel's chemical content and octane rating.

A new chemical sensor developed at ORNL can help solve these problems because of its ability to distinguish among various aviation and motor fuels, determine the presence of deicer in commercial aviation fuel (Jet A), detect ethanol in gasoline, and indicate gasoline's octane rating. The rapid fuel analyzer, developed by Barbara Hoffheins of the I&C Division and Robert Lauf of the Metals and Ceramics Division, received an R&D 100 Award in 1991. (See additional description of this development in "Technical Highlights" in this issue.)

The heart of this device is an array of tin oxide gas sensors, which each react differently to fuel vapors if no two sensors are operated at the same temperature. Each sensor's response is measured as electrical resistance, which decreases in the presence of the organic vapors being analyzed.

The collection of sensor responses to a particular fuel forms a "signature" that can be learned and later recognized by a neural network—a computer program that simulates brain nerve cells that communicate with other "neurons" through connections. After the neural network is initially taught the signatures of known fuel samples, it can almost instantly distinguish among known fuels and, by comparing signatures, guess intelligently at the identity of unknown fuels.

Lauf and Hoffheins also developed a chemical sensor that can selectively detect hydrogen leaks—a safety hazard in using, storing, and transporting hydrogen. Because the space shuttle, the orbital transfer vehicle, and the national aerospace plane use hydrogen fuel, they must have reliable systems to locate hydrogen leaks on the ground and in flight.

The hydrogen sensor operates on the principle that, when hydrogen contacts the surface of palladium, the hydrogen molecule dissociates into atoms that diffuse rapidly into the palladium. The presence of dissolved hydrogen increases the electrical resistance of the palladium. By measuring the resistance change, the concentration of hydrogen in the surrounding atmosphere can be determined.

Compensation for changes in the atmospheric temperature is achieved by using a resistance bridge in which all four legs are palladium thin films. One leg is exposed to the atmosphere, and the other three are covered by an impermeable layer. Because changes in the palladium's resistance as a result of temperature changes will affect all legs equally, the bridge voltage is insensitive to temperature fluctuations. The resistance of the uncovered leg increases over that of the covered legs only when hydrogen is present; this difference is measured by the bridge voltage. The technique for making palladium thin films for the sensor was perfected by Pam Fleming of the Solid State Division.

Our sight, hearing, and senses of touch, taste, and smell give us a clue about the materials in our environment. However, sometimes we need the products of technology to extend our senses. Such sensors and detectors developed at ORNL and elsewhere make us more aware of the threats to our health and safety, including radioactivity, high-frequency electromagnetic fields, toxic gases in the air, fuel leaks, and even drunken burglars.

Bob Lauf and Barb Hoffheins show the components of their newly developed rapid fuel analyzer, which received an R&D 100 Award in 1991 and resulted in their election to the Inventors Clubs of America International Hall of Fame.

New Light on Measuring Temperature

By Mike Cates

"ORNL's Applied Technology Division has turned to fluorescing paints to reveal the temperatures of hot surfaces in operating centrifuges and engines."

In our effort to understand the physical world around us, no attribute of nature is more important than temperature. When we measure the temperature of some object, we are determining the amount of motion (or kinetic energy) of the molecules in that object. Even though the idea of temperature is simple, its effects are complex and must be taken into account, especially when we begin to change the environment around us by building houses, roads, cities, automobiles, electronic devices, and numerous other industrial products.

The more complicated the changes we try to make in nature, the more important understanding temperature becomes. Essentially all industrial processes—from steelmaking to fabricating silicon chips for computers—require precise control of temperature. Industrial processes are simpler to understand than many natural processes, such as changes in the weather, the evolution of stars, and the functioning of our bodies, all of which also depend strongly on temperature. Because of the desire to understand, and perhaps even change, those natural processes, some people study meteorology, astrophysics, or medicine. To know the temperatures needed to control or influence the many processes that drive our civilization, we must be able to measure those temperatures without significantly interfering with the process.

ORNL's Applied Technology Division (ATD) at the K-25 Site has been involved in specialized temperature measurements since 1982. For some projects we have also collaborated with other divisions at ORNL (in particular Instrumentation and Controls and Engineering Technology), and with other DOE laboratories and several universities. We consider this research area to be an important aspect of a photonics initiative being developed for ORNL. Besides me, the ATD team studying this subject includes Steve

Bob Johnson sets up a monochrometer to select the temperature-dependent phosphor wavelength for an experiment in temperature measurement. For some phosphors, the fluorescence changes considerably with changing temperature.

Allison, David Beshears, Gary Capps, Bob Johnson, Jeff Muhs, Matt Scudiere, Bart Smith, and Ken Tobin. Our ATD group is applying its scientific and engineering expertise to situations where measuring temperature is especially important and difficult. In many situations the surface or volume of interest may be inaccessible to a regular thermometer or some other common gauge such as a thermocouple. For example, the surface in question may be in a strong magnetic, electric, or radiation field, or it may be surrounded by a very hot zone such as a burning flame or furnace. In such situations, we have found that the temperatures of samples can be effectively measured using phosphors.

Converting Fluorescence to Temperature

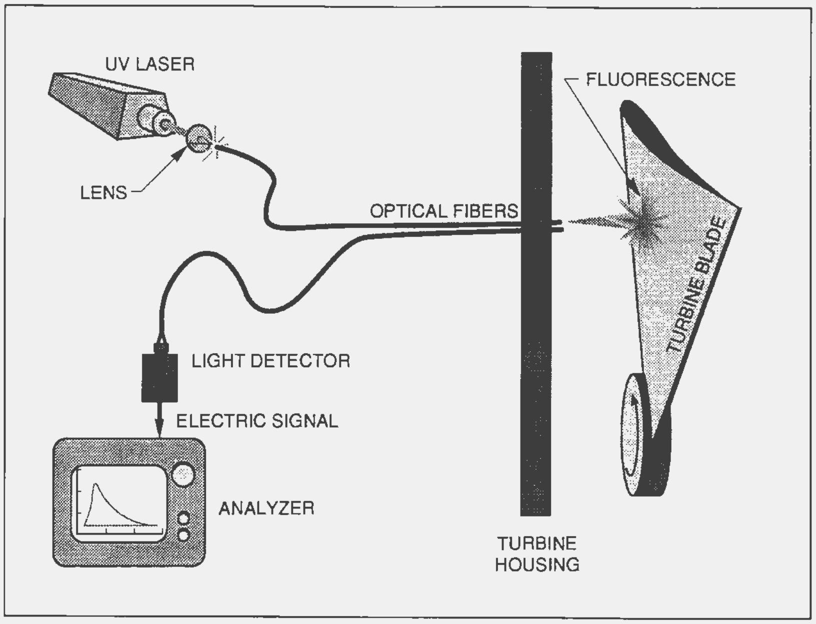
Phosphors are materials that fluoresce when excited by a source such as ultraviolet (uv) light. The amount and duration of light emitted by a phosphor usually depend on its temperature. Some materials have a very strong dependence of this kind—that is, their fluorescence changes considerably with changing temperature. Called *thermographic phosphors*, such materials, when subjected to intense laser light, provide a most important tool for special temperature measurement.

Some of the best thermographic phosphors were developed for use in color television screens. An example of a highly effective temperature-measuring phosphor of this type is a substance containing yttria (yttrium oxide, or Y_2O_3), which is used to produce red on most color TV screens. Pure yttria is not a phosphor, but it can be made into one by chemically adding a few atom percent of another metal. The added element, called a dopant or activator, replaces some of the Y atoms. In this case, the dopant is europium (Eu). The resulting phosphor consists of crystals of Eu_2O_3 scattered among crystals of Y_2O_3.

Because the Eu atoms are so widely separated from each other, they act somewhat independently; consequently, when the electrons in the Eu atoms are excited by uv light, they tend to settle back into lower energy levels (orbits closer to the nucleus) than they were in before

Steve Allison adjusts the fiber-optic collector of light from a pulsed nitrogen laser used to stimulate phosphor fluorescence.

This is a typical setup for a phosphor fluorescence experiment.



lattice cloud of electrons, "forgetting" to de-excite itself normally by emitting a fluorescence photon. This "competition" for electrons between the atoms and the lattice electron clouds produces the temperature-dependence in fluorescing phosphors. The fewer the number of electrons that take the "normal" fluorescence path, the weaker the fluorescence and the shorter its persistence time. Thus, higher temperatures can be correlated with weak fluorescence of short duration; conversely, strong and persistent fluorescence can be correlated with lower temperatures.

they became excited. As a result, they give up energy by emitting photons of light—fluorescence. Because a number of energy levels are present in any dopant that might be used, the fluorescence is emitted in a spectrum of wavelengths, or colors. The top figure on p. 50 shows a typical spectrum from the europium ions in europium-doped yttria.

The europium-doped yttria phosphor has a temperature-measuring ability because the dopant atoms do not act completely independently of their atomic environment. In particular, the surrounding molecular lattices of the Y_2O_3 crystals each have a certain behavior based on the way clouds of electrons move around the atomic nuclei in the molecules. When the europium-doped yttria phosphor is heated, the clouds of electrons absorb more energy and become excited, causing them to move farther away, on the average, from their nuclei. Because this thermal effect occurs in all atoms in this phosphor, the excited electrons in the dopant atoms "feel" the presence of the electrons in the crystal lattices around them much more strongly than before.

Sometimes, an excited dopant electron will escape from its own orbit and move out into the

How fluorescence changes with temperature in this phosphor is shown in the bottom figure on p. 50. In this case, some of the narrow emission bands are temperature active—that is, their strength and persistence depend on temperature; others are much less so, depending on the energy levels involved and the range of temperature the lattice is experiencing.

To accurately measure the temperature of a sample, we coat its surface with a very thin layer of phosphor, perhaps 10 to 50 μm thick. The coating is thick enough to produce a strong fluorescence but thin enough that its temperature will closely match that of the surface. Then, to determine the temperature, we shine uv light on the coated sample using a laser and measure its fluorescence persistence time (also called decay time). This measurement must be made quickly because the emission bands from most phosphors last for only tens of microseconds. We collect some of the fluorescence light from the band or bands of interest, measure it with a sensitive light detector such as a photomultiplier, determine its persistence time, and convert it to temperature by a calibration curve, such as that in the bottom figure on p. 50. In this way, we measure temperature without touching the surface of interest, except with uv light.

To make each special temperature measurement using phosphors, we had to solve a mystery. Like detectives, we had to study several clues to determine the best way to measure the temperature, and we had to sort through and learn to ignore pieces of confusing evidence that could lead the sleuths in our group away from the solution.

The Case of the Spinning Wall

One of our earliest measurement mysteries arose from the Department of Energy's Gas Centrifuge Program, whose aim was to design and test centrifuges for producing enriched uranium for fueling nuclear power plants. We were asked to measure the surface temperature all around the outer perimeter of a centrifuge rotating at very high speed inside a vacuum chamber. In gas centrifuges even very small temperature differences could make large differences in how efficiently the centrifuge separates the fissionable uranium-235 isotope from the nonfissionable uranium-238 isotope. Thus, we had to measure the temperature with very high precision—that is, identify temperature differences of less than a degree along a spinning centrifuge rotor.

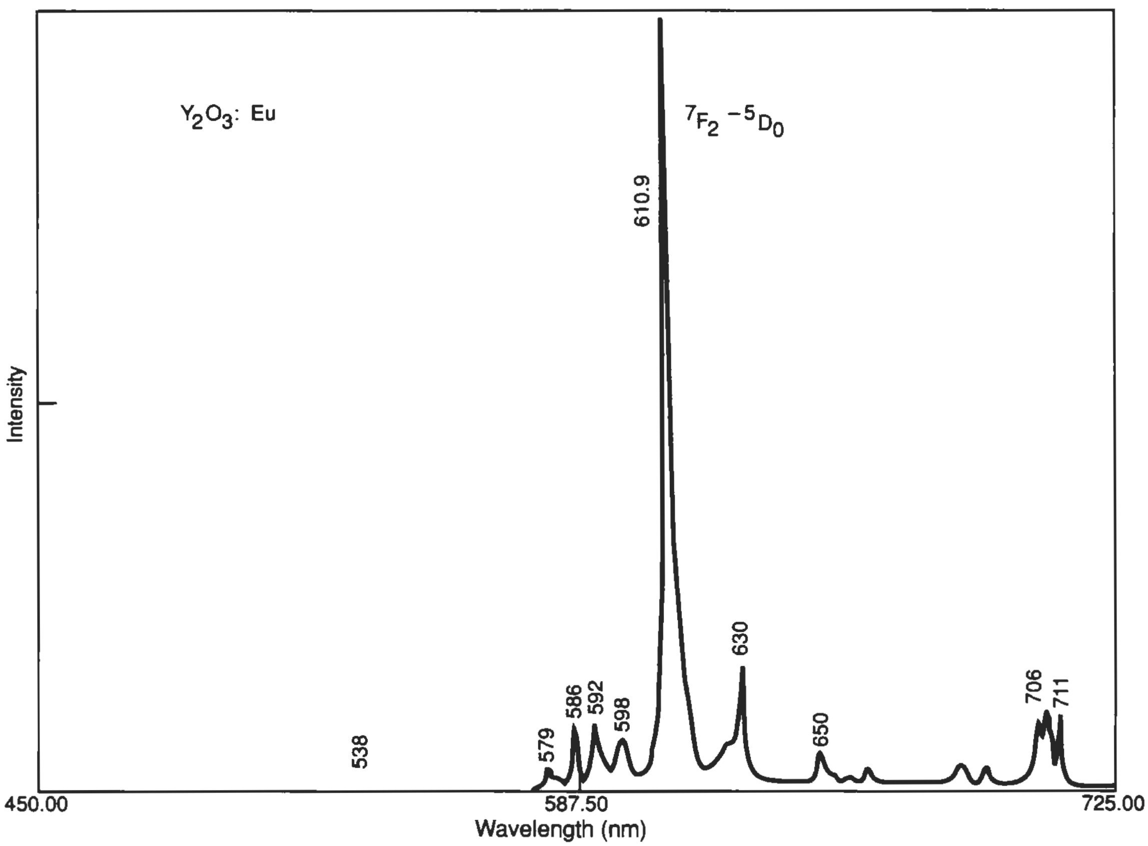
Thermocouples or pyrometric detectors would have given us confusing evidence. Thermocouples were out of the question because the large number required around the spinning rotor to obtain the necessary data would endanger its critical balance. Use of pyrometric detectors was not possible either because their response time was too long, causing the temperature differences around the rotor to blur together.

Our approach was to mix a phosphor, lanthanum oxysulfide doped with ~1% europium, into the same epoxy base used to make paint for markings on the centrifuge rotors. Fortunately, this epoxy base is transparent to uv light, permitting the phosphors to fluoresce. We then painted a stripe of the phosphor paint around the rotor at a critical height, leaving a small gap at a known azimuthal position (location in a horizontal direction around the centrifuge). The phosphor paint formed a white surface that was highly reflective when illuminated with visible light; the gap was less reflective. We placed a light-emitting diode (LED), which emitted red light, close to the rotating phosphor stripe. Using a simple optical detector to measure the LED light reflected from the stripe, we could accurately determine the location of that gap, giving an azimuthal reference.

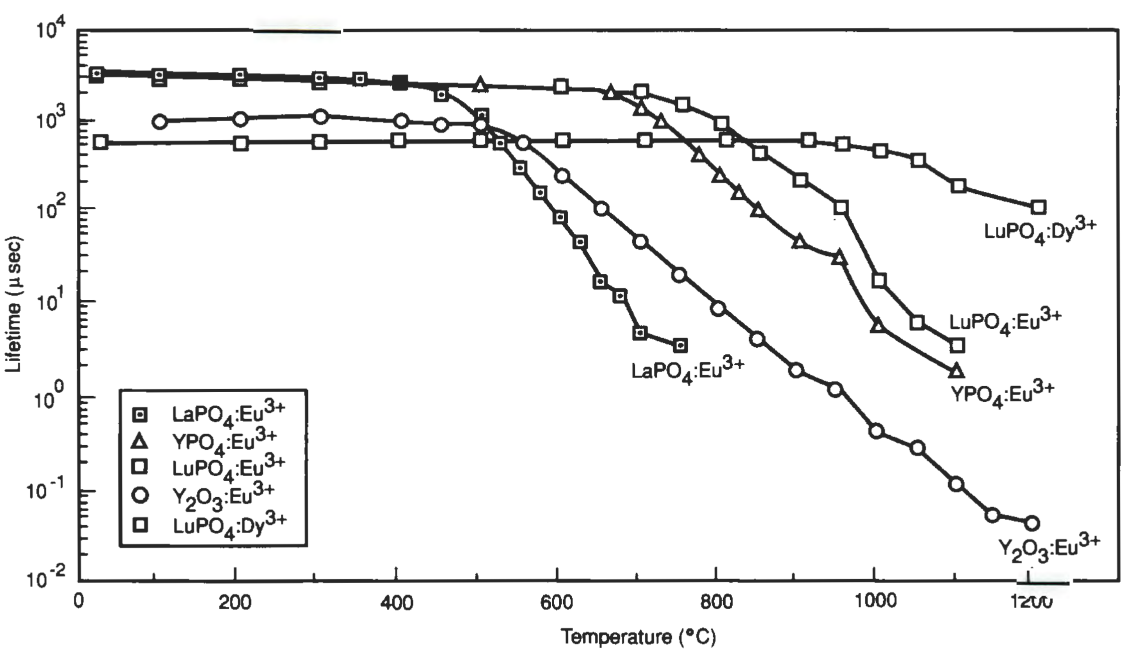
As shown in the top figure on p. 51, we used a small portable nitrogen laser (337-nm emission) to direct a uv light pulse into the optical fiber passing through the vacuum seal. Because the laser pulse was only a few nanoseconds long, it produced a sharp bright spot at a specific place on the centrifuge rotor. We triggered the laser with an electronic pulser that had an adjustable delay time, so we could control the location of the bright fluorescence spot by adjusting the time between the azimuthal reference (the gap in the phosphor band revealed by the LED) on the spinning rotor and the pulsing of the laser. Changing the time difference allowed us to "walk" all the way around the rotor with the laser pulse to measure its temperature variations.

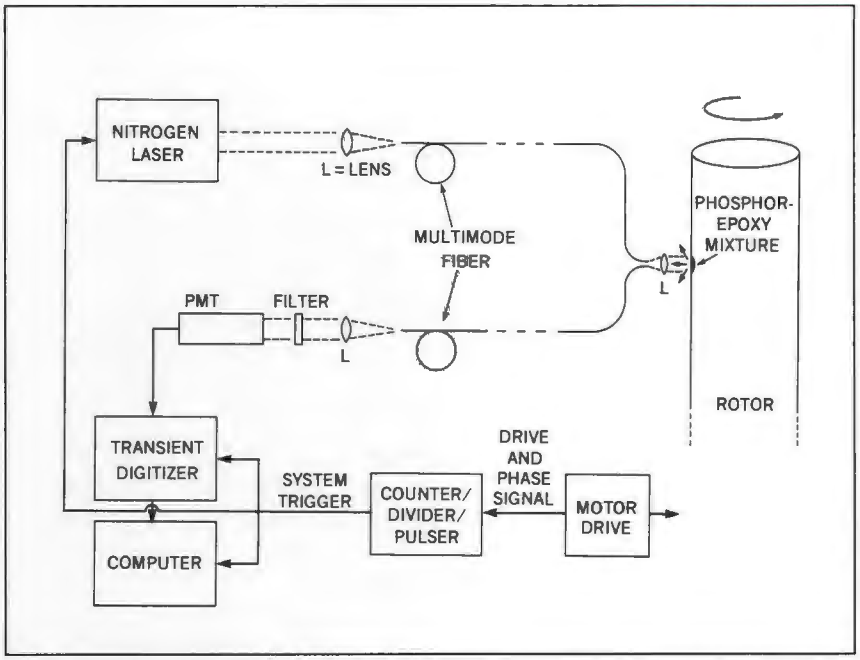
Each time the laser pulsed, the resulting fluorescence was collected by the optical fiber next to the one bringing in the laser light. The rotor was spinning so fast that the fluorescence spot moved while it was being measured. To correct for that motion, we measured the signal coming from one of the phosphor emission bands that was not temperature-active in the temperature range of the rotor and used it as a correction for the signal from the temperature-active bands. The correction, in effect, compensated for the time-dependent change in the optical field of view of the photomultiplier.

Using this approach, we measured the temperature all around the spinning rotor, as shown in the bottom figure on p. 51. Because of the sensitivity of the phosphor method, we were able to measure temperature differences as small as ~0.3°C, corresponding to a decay-time measurement precision of ~0.015 μs out of about 3 μs, or ~0.5 %. By examining the data, we found that the temperatures around the rotor varied by only a few degrees and were symmetrical, This fluorescence spectrum from europium-doped yttrium oxide shows characteristic sharp emission lines. Certain of these lines have intensities and persistence times strongly dependent on temperature.

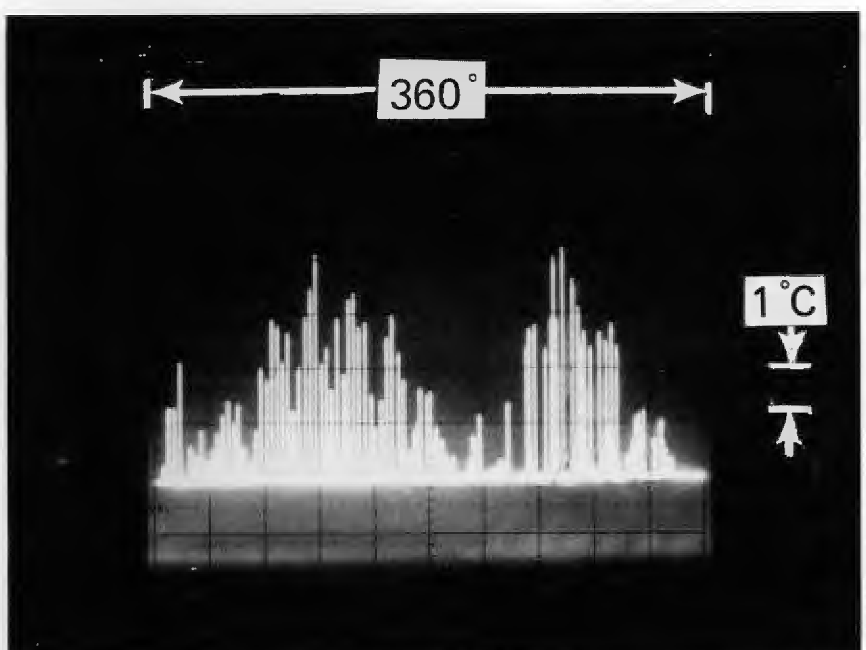


The fluorescence decay time for europium-doped yttrium oxide depends on temperature. Using calibrations of this type, temperatures can be inferred from monitoring the time-dependent emission of fluorescence light.





In this experimental setup for using fluorescence to determine centrifuge temperature, the temperature at any point around the spinning rotor could be measured.



This sample of fluorescence data from the centrifuge temperature measurement shows a regular temperature pattern with a precision of about 0.3°C.

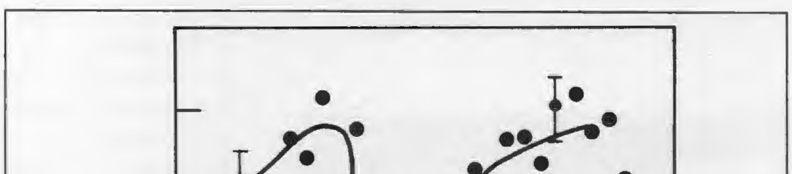
important information for the analysis of rotor dynamics.

The Case of the Cooled Surface in the Flames

Another mystery we faced was how to find the varying temperatures of a water-cooled steel surface exposed to the exhaust gases and afterburner flames from a test jet turbine engine. Researchers studying this engine at the Arnold Engineering Development Center near Tullahoma, Tennessee, needed to know these temperatures to determine whether the steel surface effectively diverted the exhaust flow and whether it was becoming hot enough to melt. The temperatures to be measured were about 1000°C lower than the air temperature around the surface.

Again, confusing evidence would be given by pyrometric or infrared measurement techniques because the huge background

This photograph shows a fluorescence flash on a steel surface bathed in the afterburner flame of an operating jet engine. The air around the surface is about 1000°C hotter than the surface itself.



This sample of data taken from the afterburner tests showed a dynamic measurement of temperature resulting from switching the afterburner on, then off, and on again.

signal from the flames would produce false readings. Furthermore, thermocouples would give misleading clues because they (1) tended to vibrate loose and fail and (2) were positioned in the internally cooled steel material, where temperature differences are large, causing an inaccurate correlation of their temperature with the surface temperature. In fact, only one of the several thermocouples installed was still functioning during our experiment.

We decided to try our fluorescence approach, and we met with good success, providing information of use to our customer. We mixed the phosphor powder in chemical binders to make a kind of spray paint that we applied to the steel surface after sanding and cleaning it. In the test arrangement, we used a frequency-tripled neodymium:YAG laser (355 nm) and associated optics to produce and collect fluorescence through a test port in the wind tunnel being used for the engine study. The top figure shows the flash of our fluorescence spot on the surface bathed in flame during the test. The measurement team obtained data (presented in the figure at left) that show the temperature changes resulting from an afterburner "excursion" in which the afterburner is turned off and then on again after a few seconds.

The Case of the Hot Turbine Vane

The mystery we solved next was how to measure the temperature of the stationary turbine vanes in a jet engine that are next to the combustion chamber where the fuel is ignited. These vanes, which are actively cooled by air diverted through their passages, must survive the highest temperatures of any surfaces within the engine. Small blockages in the cooling channels, hot spots from irregular burning of fuel, or miscalculations in the design aerodynamics could shorten the operating lifetime of the engine from thousands of hours to tens of hours, or even result in catastrophic failure. Accurate temperature measurements are needed to determine if the engine has problems that need to be addressed to ensure safe, long-term operation.

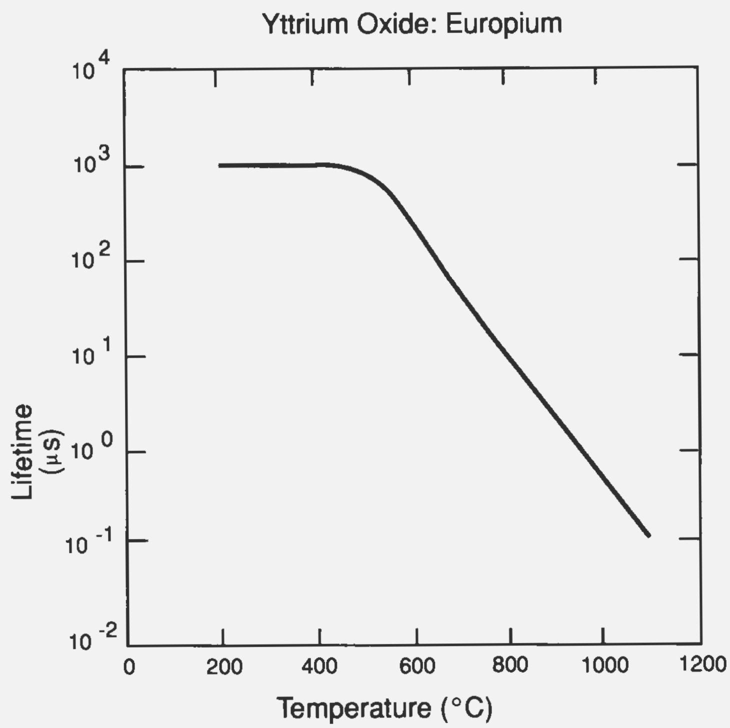
These turbine engine probes are used to measure temperature.

These vanes of a jet turbine engine were coated with thermographic phosphor for use in measuring temperature in an engine performance test.

Standard measurement techniques that use infrared emissions can be used in many areas of a jet engine. However, depending on pyrometric measurements on these vanes would produce dangerously misleading clues for our sleuths because the background from the burning fuel is too intense for an accurate measurement. Other false and quickly vanishing leads would come from thin-film thermocouples, sometimes used in engines. These devices cannot survive the temperatures reaching as high as ~1200°C. Standard wire thermocouples also would provide confusing data because they often fail from heat and vibration.

A jet engine test at Pratt Whitney Corporation in Hartford, Connecticut, once again proved fluorescence to be an accurate measure of temperature. In this effort, we collaborated with researchers from Los Alamos National Laboratory and the EG&G Measurements Laboratory in

The ORNL team measured temperatures on a turbine vane inside the engine for various engine rotation speeds.



Santa Barbara, California. The instrumentation used in the test included our division's Nd:YAG laser, optical fibers, and test probes modified here at Oak Ridge from standard pyrometry probes used in test engines.

We used two phosphor types: yttrium oxide doped with europium (Y_2O_3:Eu), and yttrium vanadate doped with europium (YVO_4:Eu). The first was used to measure temperatures ranging from about 600 to 1100°C, and the latter is for measurements ranging from about 400 to 600°C. We caused the phosphors that coated the turbine vanes to fluoresce by passing pulsed laser light through optical fibers entering the engine; then we measured the fluorescence signals leaving the engine through the fibers.

The bottom photograph on p. 53 shows the phosphor layer on one of the test turbine vanes. The hole in the test vane assembly is where the pyrometry probe was located; our modified probe was in that same location. The temperatures we measured were plotted as a function of the rotational speed of the engine. We can determine for each speed whether the test turbine vane is sufficiently cool or too hot for proper engine performance.

Outlook

Temperature-measurement mysteries continue to unfold, and ORNL's Applied Technology Division continues to be called on to solve them. The three examples show the wide variety of possible measurement scenarios. We have measured temperatures of the spinning part of a permanent magnet motor, requiring optical fiber access into a gap only a millimeter wide. We have measured temperatures of test turbine engine materials being rotated in the flame of a jet fuel burner. We have also done a similar measurement on a ceramic surface in a steam calorimeter being heated by a flame.

At the other end of the spectrum, we have measured the fluorescence of very cold surfaces immersed in liquid nitrogen and liquid helium. The full range of our temperature measurements, in fact, extends from about 8 K to about 1600 K. Anywhere along that whole temperature band one or more phosphors can be used to determine the temperature of the coated surface.

Our temperature sleuthing skills continue to improve. Our efforts have moved strongly into three major branches of thermographic technology: (1) extending the temperature range to higher levels, (2) two-dimensional or area thermometry, and (3) dynamic temperature measurement. We are experimenting with a group of phosphors that will allow us to measure temperatures as high as ~1700°C. We are also investigating the use of resonance photon absorption techniques to push thermometry up to near the material dissociation limits of the phosphors, or ~2000°C. Our two-dimensional thermometry uses video systems and image-processing techniques to convert fluorescence images into temperature maps. In our early work in dynamic thermometry, we have measured the temperature of resistance-heated wire that changes at the rate of more than 100°C/ms.

Using phosphors, optical fibers, lasers, and other sophisticated tools, we are prepared to shed light on the unsolved mysteries of temperature measurement.

Biographical Sketch

Mike Cates (left) and Steve Allison adjust the instrumentation used for a thermographic phosphor experiment.

Mike Cates is leader of the Photonics and Laser Applications Group in ORNL's Applied Technology Division. He received his Ph.D. degree in physics from Texas A&M University after doing his graduate research at ORNL under an Oak Ridge Associated Universities fellowship. Before coming to Oak Ridge in November 1980, he worked for more than 11 years at Los Alamos National Laboratory. He has extensive experience in measurement science, including use of thermal imaging, fluorescence spectroscopy, and fiber-optic sensor systems. He also has considerable experience in coordinating large-scale projects involving many types of technical expertise. He has been active in area singing and theatrical productions and has been a member of the board of directors of both the Oak Ridge Civic Music Association and the Oak Ridge Community Playhouse.

RE: Awards & Appointments

David Campbell

George Courville

Homer Yook

Herman Postma, former ORNL director who retired January 31, 1991, as senior vice president of Martin Marietta Energy Systems, Inc., has been awarded a Distinguished Associate Award by the Department of Energy. He was cited for his "outstanding leadership of and many contributions to the scientific research and development programs of DOE and its predecessor agencies."

Paul Haubenreich has received a Distinguished Associate Award from DOE for his "outstanding and dedicated leadership of the International Large Coil Task Force." According to the citation, "The successful completion of this major superconducting technology effort brings significant benefits to the fusion programs of the United States and its International Energy Agency partners and enhances opportunities for future international cooperative efforts."

David O. Campbell has received the 1991 Glenn T. Seaborg Actinide Separations Award.

James S. Bogard has been appointed to implement at ORNL the requirements of DOE's Oversight Agreement with the state of Tennessee. The agreement provides public assurance that health, safety, and the environment are protected at DOE sites.

Gene M. Goodwin has received the American Welding Society's 1991 William Irrgang Award sponsored by the Lincoln Electric Company and given to a person who has done most in the past five years to achieve the Society's goal of "advancing the science, technology, and application of arc welding."

Mike Kuliasha was the conference chairman for the DOE-ORNL Technologies for a Greenhouse-Constrained Society Conference, held June 1991 in Oak Ridge.

George Courville has received an Award for Excellence in Technology Transfer by the Federal Laboratory Consortium for Technology Transfer for his work in establishing the Roof Research Center.

Lee Shugart has been appointed a consultant to the U. S. Environmental Protection Agency's Science Advisory Board. He also has been named main editor of the scientific journal *Ecotoxicology*.

Tom Kress has been appointed a member of the Advisory Committee on Reactor Safeguards of the Nuclear Regulatory Commission.

Chester R. Richmond has been appointed a member of the National Advisory Council for Technical Education.

Donald B. Hunsaker has been elected president of the National Association of Environmental Professionals. He was recently appointed technical assistant to **David Reichle**, associate director for Environmental, Life, and Social Sciences.

Homer Yook has been named head of the newly formed Technology Applications and Resource Management Section of ORNL's Robotics and Process Systems Division.

Shirley G. Lawson has received a Distinguished Achievement in Administrative Support Award from ORNL's Environmental Sciences Division.

Laura McDowell-Boyer has been named a consultant to the Cleanup Subcommittee of DOE's Advisory Committee on Nuclear Facility Safety.

Carla Gunderson received the Distinguished Achievement Award for Technical Support from ORNL's Environmental Sciences Division. She was cited for "uncompromising commitment to accuracy in collecting and analyzing data and her thoroughness in publishing the results."

Richard L. Heestand has been elected a fellow of the ASM International for his "significant contributions to the development of advanced alloys used in energy systems, national defense, and space exploration."

Fred W. Meyer has been elected a fellow of the Division of Atomic, Molecular and Optical Physics of the American Physical Society.

Margaret B. Emmett has been elected chairperson of the Oak Ridge–Knoxville Section of the American Nuclear Society.

Bruce L. Kimmel has been appointed to the Scientific Review Panel for the National Science Foundation's Experimental Program To Stimulate Competitive Research.

Marilyn A. Brown has received the Gold Medal Award for the best paper published in 1989–1990 in the *Journal of Technology Transfer*. The paper, coauthored by C. Harvey Major of DOE, is entitled "Technology Transfer Strategies of DOE's Conservation Programs."

Milton Russell has been named chairman of a National Research Council study of options for disposal of hazardous wastes.

Kowetha A. Davidson has been appointed to the Technical Reports Review Subcommittee of the National Toxicology Program Board of Scientific Counselors.

Todd Anderson received the 1991 Graduate Student Paper Award from the Environmental Chemistry Division of the American Chemical Society.

Frank Southworth has been elected director of the Energy Specialty Group of the Association of American Geographers.

Michael S. Bronzini has been selected chairman of the Committee for the Study on Landside Access to U. S. General Cargo Ports. This is a committee of the Transportation Research Board of the National Research Council. He has also been appointed to the Advisory Committee for the Vanderbilt Engineering Center for Transportation Operations and Research at Vanderbilt University.

David L. Greene has been appointed a member of the Committee on Fuel Economy of Automobiles and Light Trucks of the Commission on Engineering and Technical Systems of the National Research Council.

Cheng Liu is a co-winner of the 1991 Applied Geography Citation Award from the Association of American Geographers for his work on the Bangladesh Transportation Modeling System.

John M. Bownds has received the Hal Foss Award of the National Association for Search and Rescue for his contributions to the organization.

Thomas J. Wilbanks has been elected vice president of the Association of American Geographers. As president of the organization in 1992–1993, he will host the International Geographical Congress in August 1992 in Washington, D. C.—the first such congress in the United States in 40 years.

Thomas P. Burns, a DOE Hollaender Fellow in ORNL's Environmental Sciences Division, has received the Robert C. Anderson Memorial Award from the University of Georgia Research Foundation.

Anne Hoylman, a Ph.D. student in ORNL's Environmental Sciences Division, has received the Science Alliance Award from the University of Tennessee's Environmental Biotechnology Section.

James R. Sand and **Edward A. Vineyard** received an ASHRAE 1990 Best Paper Award from the American Society of Heating, Refrigerating, and Air-Conditioning Engineers for their paper, "Experimental Performance of Ozone-Safe Alternative Refrigerants."

Earl McDaniel has been awarded a plaque in recognition of his waste management contributions at the 10th Annual Incineration Conference, organized by the University of California at Irvine.

John C. Miller has been named a fellow in the Optical Society of America.

Paul Rohwer is treasurer of the Health Physics Society and served as the president-elect of the American Academy of Health Physics (AAHP), of which **Jim Turner** is the president-elect.

Barry Berven is president of the Environmental Radiation Section of the Health Physics Society and chairs its Standards Committee.

Robert Reed, formerly of the Environmental Sciences Division, has been named head of the Integrated Analysis and

Marilyn Brown

Kowetha Davidson

Michael Bronzini

Mark Janney

Lawrence Barnthouse

James Stiegler

Assessment Section of ORNL's Energy Division.

Edward D. Aebischer has been named manager of ORNL's University and Educational Programs.

David Mullins has been elected vice president of the Tennessee Valley Chapter of the American Vacuum Society.

I. Busch has received a Eugene P. Wigner Fellowship.

H. E. Knee has been named a member of the Executive Committee of the Human Factors Division of the American Nuclear Society.

The East Tennessee Chapter of the Association for Women in Science has given its Distinguished Scientific Achievement Award to **Monica G. Turner;** its AWIS Service Award to **Julia A. Watts;** and its Outstanding Leader and Advocate Award to **Annetta P. Watson.**

R. C. Gwaltney has been elected a fellow of the American Society of Mechanical Engineers.

Cindy Robinson has been elected president of the East Tennessee Chapter of the Society for Technical Communication.

Louis K. Mansur has been named American editor of the *Journal of Nuclear Materials.*

Richard A. Strehlow has been named co-chair for a symposium on "Standardizing Terminology for Better Communication."

Paul F. Becher has received a Humboldt Research Award from the Alexander von Humboldt Foundation.

Al Geist and **V. Sunderam** have received first prize in the Computer Science Division of the national 1990 IBM Supercomputer Competition for their entry "The PVM System: Supercomputer Level Concurrent Computation on a Network of IBM RS/6000."

The ORNL team that developed the **Laboratory Telerobotic Manipulator** received an Outstanding Engineering Achievement Award from the Tennessee State Society of Professional Engineers.

Numerous ORNL employees were honored for outstanding accomplishments in research, management, and operational support activities at the annual Martin Marietta Energy Systems Awards Night, held May 24 in Knoxville. Three ORNL employees singled out for top awards who later received the Jefferson Cup Award at Martin Marietta Honors Night Ceremonies were Inventor of the Year **Mark A. Janney,** for developing a gelcasting process for near-net-shape fabrication of ceramic components that should lower fabrication costs; Author of the Year **Lawrence Barnthouse,** for work on a new framework for analysis of risk from toxic contaminants to fish; and Operations Improvement Award recipient **James O. Stiegler,** for management of model programs for environment, safety, and health and for quality in the Metals and Ceramics (M&C) Division, which he manages. Members of the Atomic Trades and Labor Council (ATLC) contingent at ORNL also were cited for contributions by the bargaining unit personnel to efforts to prepare for and respond to findings in the DOE Tiger Team assessments. The award was accepted by ATLC president Robert G. Keil.

ORNL employees who received an Operations and Support Award, which recognizes significant improvements to efficiency, major cost avoidance or cost reduction efforts, innovations that enhance programmatic operations, and extraordinary personal effort in support of major projects and goals, are **E.C. Brown,** for outstanding commitment to company values through participative management and concern for others in providing strong leadership to the Security Patrol; **Gary M. Denton,** for exemplary leadership of the Performance Improvement Process and Values Committee and in coordinating the Martin Marietta corporate audit; **Jean Disney,** for providing leadership that is recognized company-wide in compensation issues and for processing changes in salaries and status for staff; **Rick J. Forbes,** for demonstrating a sustained commitment to excellence in the development of health and safety upgrades; **Amy Harkey, Marilyn V. Ayers, Billy L. Barnett, Sherry P. Ketterer, Lola M. Roseberry, Ada Thompson, Rebecca A. Wilker,** and **Scott D. Wilson,** for noteworthy publications and document management support to DOE's Tiger Team assessment; **Alma Hawkins,** for providing exceptional secretarial services in the M&C Division while on assignment to the Tiger Team assessment; **Frank C. Kornegay,** for contributions to the development of an atmospheric sampling, monitoring, and modeling system to achieve compliance with Tennessee, EPA, and DOE requirements; **Darrell Mongar,** for achieving recognition as the Energy Systems 1990 Security Inspector of the Year and for ranking fourth nationally in DOE annual Security Inspector of the Year competition; **Carol Moorhead,** for outstanding operational performance and for contributions to ORNL and its mission through exemplary performance; **Waldean Richardson,** for outstanding leadership and dedication in organizing and executing administrative support functions for ORNL's Research Reactors Division; **Paul W. Shearer, William S. Akers, Jr., J. Lynn Anderson, Sandy J. Bolinsky, Doris P. Brooks, M. Brad Graves, Jerry B. Hunt, Ava J. King, Sandy Lowe,** and **Paul S. Rohwer,** for developing and implementing an innovative internal health physics technician training program to meet a critical company need and provide new career opportunities; **Myint Thein, Benito Gonzalez Dominguez,** and **Roger D. Myers,** for significant improvements in ORNL Radiobioassay Laboratory comprehensive quality control measures and use of efficient and accurate procedures through superior performance in pilot testing for the DOE Laboratory Accreditation Program; and **Alice Wittmer,** for outstanding performance in single-handed management of administrative components while serving as secretary to two major organizations during the Tiger Team assessment.

Three ORNL employees received the Management Achievement Award, which recognizes exemplary leadership, achievements in dealing with resource limitations and other constraints, and specific accomplishments within the year or sustained excellent performance over a long period. They are **John Sheffield,** for tireless efforts in leading the self-assessment process, which not only met the Tiger Team assessment requirements but laid the foundation for continuing self-assessment; **W. D. Shults,** for superior leadership of the Analytical Chemistry Division and for management contributions to the Laboratory and the company; and **Jerry H. Swanks,** for recognized leadership prior to and during the Tiger Team audit and for significant contributions to ORNL's success in the activity.

ORNL employees who received the Technical Achievement Award, which is given for excellence in research or engineering, inventions with realized or potential value to the company or its customers, and authorship of significant published materials, are **Steve Allman** and **Ronald C. Phillips,** for development of an in situ monitor for preparation of superconductive films and for innovative contributions to freon detection; **Lawrence W. Barnthouse, Aaron E. Rosen,** and **Glenn W. Suter II,** for publication of "Risks of Toxic Contaminants to Exploited Fish Populations: Influence of Life History, Data Uncertainty and Exploitation Intensity"; **Paul Becher, Kathleen Alexander, Peter Angelini, Chun-Hway Hsueh, Hua-Tay Lin,** and **Terry Tiegs,** for development of a fundamental understanding of the crack-bridging mechanisms to improve the toughness and mechanical performance of fiber-reinforced ceramic composites; **Kenneth S. Blakely,** for processing of iridium sheets, iron aluminides, and superconducting ribbons and for training staff in the use of KCN and acid-room procedures; **Gerard J. Bunick,** for the crystallization of nucleosomes, the fundamental structural unit in chromatin, as a homogeneous structure for crystallographic analysis at near-atomic resolution; **Sylvester W. Cook,** for outstanding performance in operating, upgrading, and maintaining the multiple-ion facility, which is the mainstay of ORNL's radiation effects and ion-treatment programs; **C.S. Daw, Ned E. Clapp, Jr., Darryl J. Downing,** and **William F. Lawkins,** for noteworthy leadership of a multidivisional team that established chaotic time series analysis as a new research area at ORNL; **Barry C. Grant,** for preeminent operation and technical support relating to explosives-detection projects and for outstanding contributions toward compliance with the Occupational Safety and Health Administration's chemical-laboratory regulations; **Jeffrey H. Harris,** for sustained and exemplary personal and collaborative contributions to the study of fluctuations in stellarator plasmas; **Howard Haynes,** for outstanding contributions toward the development of several innovative techniques for monitoring safety system valves used by nuclear utilities; **W. P. Huxtable** (Technical Operations), **Alicia Compere, John Googin** (Y-12 Plant), and **William L. Griffith,** for outstanding performance in a project that doubled the aluminum nitrate recovery rate in the Y-12 Nitrate Recycle Facility; **Mark A. Janney** and **Ogbemi Omatete,** for development of a novel gelcasting process, which should lower the cost of advanced ceramics fabrication; **Cornelius E. Klots,** for the development of kinetic methods for quantifying magic in atomic and molecular aggregates; **Douglas H. Lowndes, John Budai,** and **David P. Norton,** for publication of "Superconductivity in Nonsymmetric Epitaxial YBaCuO/PrBaCuO Superlattices: The Superconducting Behavior of Cu-O Bilayers"; **Ben McConnell, Vincent W. Campbell, Robert A. Hawsey, W. K. Kahl, Martin Lubell, J. N. Luton, Jr., S. William Schwenterly,** and **Carl W. Sohns,** for leadership and technical contributions to the design, construction, and testing of a novel axial gap, variable-speed, alternating-current, low-temperature superconducting motor; **Paul Menchhofer,** for conversion of the patented gelcasting process into a complex extrusion apparatus; **Wilfred M. Post, Virginia H. Dale, Donald L. DeAngelis, William R. Emanuel, Anthony W. King,** and **Tsung-Hung Peng,** for publication of "The Global Carbon Cycle"; **G. R. Satchler,** for publication of "Heavy-Ion Scattering and Reactions Near the Coulomb Barrier and 'Threshold Anomalies'"; **P. C. Srivastava,** for publication of "A New Conjugating Agent for Radioiodination of Proteins: Low In Vivo Deiodination of a Radiolabeled Antibody in a Tumor Model"; **Peter J. Todd,** for design, construction, and general development of an organic secondary ion microprobe for obtaining micrographs of biological tissue; **G.R. Wetherington, Jr., Robert Tate, R. Wesley Wysor,** and **William D. Zuehsow,** for leading a team that developed a unique state-of-the-art system for qualifying the operational acoustic signatures of U.S. Navy submarines; **Thomas L. Wilson, Jr., Ronald E. Battle, Roger A. Kisner,** and **Carlos March-Leuba,** for design of the plant control system for Babcock and Wilcox reactors, thus successfully transferring some of the ORNL-developed control technology to private industry; **Patrick Worley,** for publication of "The Effect of Time Constraints on Scaled Speedup"; and **Steven J. Zinkle** and **E. H. Lee,** for publication of "Effect of Oxygen on Vacancy Cluster Morphology in Metals."

This award-winning scanning electron micrograph by Mukund Rao and Jim Keiser shows a crater produced on an aluminum surface by the impact of a single spherical particle of tungsten carbide propelled at 661 m/s by helium in a light-gas gun.

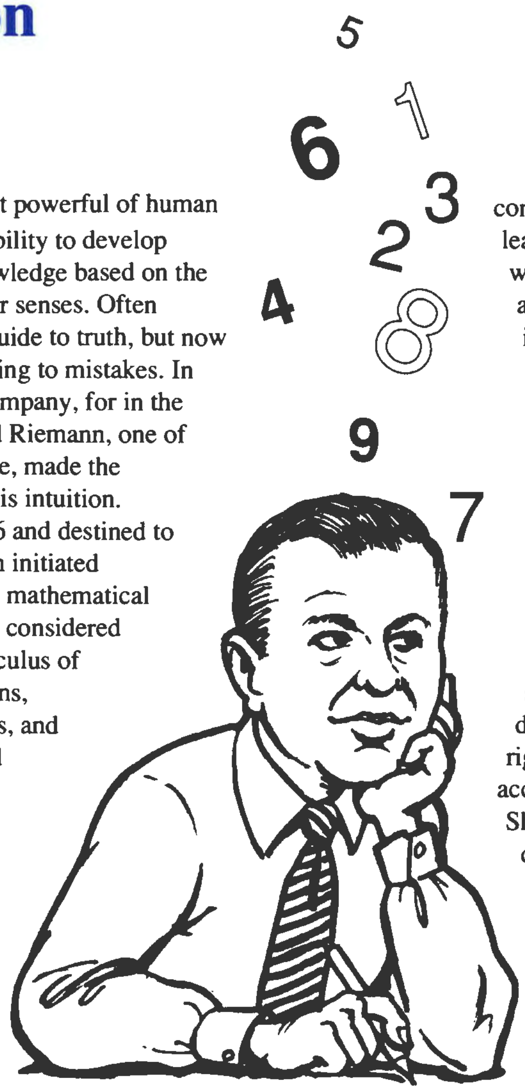
Mukund Rao and **James Keiser** placed first in the Wear Photomicrograph Competition of ASM International for their photograph of magnified objects associated with tribology, the study of friction and wear.

Intuition, Rigor, and Bernhard Riemann's Dissertation

by Alan Solomon

One of the most powerful of human tools is our ability to develop intuitive knowledge based on the information provided by our senses. Often intuition can be a reliable guide to truth, but now and then it will fail us, leading to mistakes. In this case, we are in good company, for in the mid-19th century, Bernhard Riemann, one of the giants of modern science, made the mistake of overly trusting his intuition.

Born in Germany in 1826 and destined to live only 40 years, Riemann initiated major work in almost every mathematical discipline. As a result, he is considered a founding father of the calculus of variations, complex functions, partial differential equations, and real analysis. Theorems and methods for solving key problems in electrical engineering, heat transfer, acoustics, and numerous other fields bear his name.



In 1851 Riemann completed his doctoral dissertation at Göttingen. This dissertation is a landmark of science, because it establishes the basis for a broad spectrum of fields and methods for solving problems including finite element methods in problems of structures, characteristic methods for numerically solving wave propagation problems, and conformal mapping methods for steady-state heat transfer processes.

To a large extent his dissertation rests upon a single assertion referred to as "Dirichlet's Principle" (after Riemann's teacher Peter Dirichlet). In rough terms Dirichlet's Principle concerns finding the surface of least area spanning a given wire frame, and Riemann appealed to geometric intuition to state that this simple problem had a solution. His dissertation was accepted, and its results were applauded widely and used—but only for a while.

Until 1854, Karl Weierstrass (1815–1897) was an obscure instructor at a German high school. Weierstrass belonged to that school of mathematicians demanding mathematical rigor and resisting automatic acceptance of the "obvious." Shortly before Riemann's death, Weierstrass discovered a flaw in Dirichlet's Principle. The flaw is akin to asserting that "zero is the smallest positive number." This simple statement does not make sense because zero is not positive and is at the same time the largest number less than every positive number.

"Bernhard Riemann, one of the giants of modern science, made the mistake of overly trusting his intuition."

Riemann attempted to correct this error as did many others because of the intuitive correctness of the results of his dissertation. However, these efforts came to naught until David Hilbert's proof in a five-page paper in 1905, giving rise to the entirely new field of functional analysis.

A popularly written description of Riemann's error appears in the biography of David Hilbert by Constance Reid.

Students Help Solve ORNL Waste Problem

This past summer university students conducted research for a waste minimization project using beadlike inorganic ion exchangers to remove radionuclides from liquids. From left: Chris Lockwood, Brian Dodson, Omaira Melendez, Bill Chase, Robin Bright, Jack Collins (supervisor), Debbie Davidson, and Allen Boatman.

Summer at ORNL brings a flood of fresh faces as high school, college, and graduate students come to the Laboratory for the chance to do hands-on research. Most of these students work for several months with a team of ORNL scientists, but the Chemical Development Section (CDS) in the Chemical Technology Division (Chem Tech) is doing something different.

For several years, students alone have conducted the experiments for a potential new method of waste minimization. "I find it amazing that this many students have come together to work on such an important development," says Chris Lockwood, an undergraduate student at the University of Kentucky.

During the summer of 1991, eight students helped to develop and characterize beads of inorganic ion exchangers that remove radionuclides from liquid waste, thus minimizing the amount of liquid that must be disposed of as high-level radioactive waste. This project was proposed by Chem Tech researchers to minimize radioactive waste at its source.

In the spring of 1990, it was learned that the use of hot drains for disposal of radioactive liquid wastes from the 4500-area buildings and others might be prohibited to prevent contamination of ORNL streams. In response, Jack Collins and Morris Osborne, both of Chem Tech, suggested a Performance Improvement Process (PIP) project to find an effective way to remove the radionuclides from the liquid wastes generated by their laboratories.

The ion exchangers proposed by the PIP committee are made of hydrous oxides or monohydrogen phosphates of zirconium, titanium, iron, and aluminum. Because these beads attract, concentrate, and remove the radioactive materials from the liquid, high-level liquid waste is converted to low-level liquid waste, which can be disposed of more safely. The beads, or microspheres, are stable and easy to handle, making them a preferred disposal form for highly radioactive materials.

At first, the CDS employed a student from Tennessee Technological University (Tennessee Tech) to help Collins develop the microspheres. Collins enjoyed the experience of working with young people and saw the need for more help, so the CDS, with help from Oak Ridge Associated Universities (ORAU) and Chem Tech student coordinator Jonathan Woodward, hired more students. These efforts provided all the initial labor because the project had no funding to support Laboratory employees.

Students employed during the summer of 1991 included

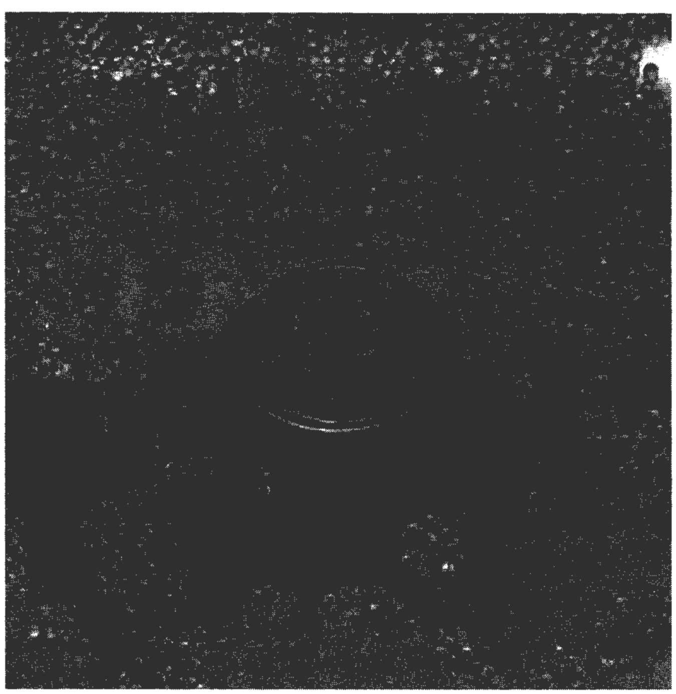
- Allen Boatman and Bill Chase, technicians from Pellissippi State Technical Community College;
- Deborah Davidson, who is working on a master's degree from Tennessee Tech;
- Robin Bright and David Glasgow, summer contractors from Tennessee Tech;
- Brian Dodson, a summer ORAU student from the University of Tennessee at Chattanooga;
- Omaira Melendez, a summer student from Lincoln University in Pennsylvania; and
- Chris Lockwood, a co-op student from the University of Kentucky.

Each student worked on a specific task concerning the ion exchangers; for example, Davidson studied the effect of acidity (pH) changes on the percent removal of radionuclides from the waste stream, and Melendez tried to convert hydrous metal oxides to phosphates that will also work as exchangers. "We basically had our own projects," Davidson said, "but we also interacted a lot during discussions, which helped me understand the importance of my work." Bright, who tested exchangers made of sodium titanate for uptake of radioactive materials, said, "It's a great group to work with. I want to come back again next summer!"

Students who formerly worked on the project included

- John Hunley, a co-op student from Tennessee Tech, who was here in 1989 and 1990;
- Anna Edwards, a 1990 summer contractor from Tennessee Tech; and
- Stephen Pye, a co-op student from the University of Tennessee, who worked during the spring of 1991.

Dale Ensor of Tennessee Tech participated with Collins and section manager Dave Pruett in overseeing the bead loading and characterization studies conducted by Davidson, Bright, Edwards, and Glasgow.



These wet hydrous titanium oxide beads are pictured next to a penny for scale.

Omaira Melendez, a student from Lincoln University in Pennsylvania, and her supervisor Jack Collins study some of the phosphate ion exchangers she produced from hydrous metal oxide beads. Both bead forms have proven very effective in removing radionuclides from certain waste streams.

The best exchangers are determined experimentally, so students in the lab have been constantly testing new combinations of ingredients to make different ion exchangers. "At ORNL we're trying to develop as many exchangers as possible that can be used for a variety of radionuclides," says Collins.

To remove radionuclides from liquid waste that originated in a hot cell or laboratory, the beads are placed in a stainless steel mesh wire basket inside a canister. The liquid waste is poured into the canister and air-stirred so it passes through the beads.

High-level radioactive solutions are thus converted to low-level liquid waste that can be removed from the hot cell and sent to the waste-management evaporator for further treatment. The beads, once loaded with the radioactive cations, can be dried to remove any water, sealed off, packaged, and sent to a burial site for high-level radioactive waste. "The leachability of the radionuclides from the beads is extremely low," says Collins, "making them a relatively safe and simple form of disposal."

Ion exchange occurs when a cation (positively charged ion) of the exchanger is replaced by a cation of the radioactive material. Different radioactive elements, such as cesium-137 and americium-241, require different types of ion exchangers. "Each radioactive solution dictates that a certain type of exchanger be used," explains Collins. For example, zirconium monohydrogen phosphate beads have been found to be very effective in removing cesium-137 from a waste stream. Hydrous titanium oxide works well for removing uranium, even from strong salt solutions.

Inorganic ion exchangers in the form of microspheres are a research interest unique to ORNL. It has been known since the 1960s that certain inorganic materials have an affinity for and tendency to absorb radioactive elements. However, these ion exchangers were previously available only as fine powders or granular material that tended to degrade into fine particles. The powders were not practical for use in large-scale treatment of waste streams because they plugged up ion-exchange columns.

Searching for a better exchanger, Collins and Pruett decided that producing certain inorganic ion exchangers as gel spheres would be a more practical approach. "It's an idea that is really breaking ground and could be a big thing in waste cleanup techniques," said Chase. "I'm lucky to have been involved with it."

Students made the microspheres by the internal gelation process originally used at ORNL for making nuclear fuel. Lockwood and Dodson determined the combinations of "ingredients" and process parameters that make beads gel properly. "We ruled out everything that didn't work, leaving us with the best recipes for beads," said Dodson. Toward the end of the summer, they and Collins became involved with patenting the microspheres. Chase and Boatman were the student technicians—or, as they called themselves, the "bead men"—who redesigned the laboratory equipment used in making the beads to improve production rate. At first, only around 200 mL of beads could be made during one run of the equipment; later, that number rose to 822 mL. Boatman was responsible for setting up a second laboratory primarily to make beads of titanium compounds.

Jimmy Bell, head of the CDS, is excited about the waste minimization potential of this technology and about the students' involvement. The beads are already being used to remove radioactivity from waste streams from hot cells and labs within the section, and the Metals and Ceramics and other divisions have shown interest in adapting the technology to their own facilities. Says Bell, "It takes both science and artistry to invent a technology that requires a lot of experimentation and inquisitiveness. Jack Collins is both a chemist and an artist."

It seems that his students are too. "The students keep better log books than many researchers do," says Collins. Their involvement has been the primary source of technical support for the PIP project. They also bring enthusiasm and new ideas. "I'm finally learning the point of taking all those classes," says Dodson. "ORNL is a nice mixture between industry and university settings. It's academic but goal-oriented at the same time." While the students experienced what it's like to be researchers at a national laboratory, ORNL is benefiting from their contributions. Bell's section has hired Boatman and Chase as technicians and will continue its relationship with other students. The Chemical Development Section has shown the importance of the ORNL-student connection.

—*Alexandra Witze,* ORNL Review *summer intern and senior at the Massachusetts Institute of Technology.*

Arsenic and Old Zach

Larry Robinson and Frank Dyer examine a sample of hair removed from the body of former U. S. President Zachary Taylor. The researchers analyzed hair and nail samples for arsenic to determine whether Taylor was poisoned. The samples were irradiated in ORNL's High Flux Isotope Reactor and examined by neutron activation analysis. The results of analysis, sent to a Kentucky coroner, indicated no abnormal levels of arsenic.

In June 1991, ORNL received the 12th U. S. president at the High Flux Isotope Reactor (HFIR)—well, parts of him, anyway. Some of Zachary Taylor's remains were analyzed for arsenic, using the HFIR, to determine whether he was the first U.S. president to be assassinated. Taylor died on July 9, 1850, several days after attending the Independence Day dedication of the Washington Monument. At the time, his death was attributed to gastroenteritis, an inflammation of the lining of the stomach and intestines.

Recently, however, an author researching a book on Taylor theorized that he was poisoned by political rivals because he opposed the spread of slavery into the southwest territories. ORNL was chosen to help solve the mystery of Taylor's death by testing samples of hair and nails taken from his remains in Louisville, Kentucky. But researchers from ORNL's Analytical Chemistry Division, Larry Robinson and Frank Dyer, found no elevated levels of arsenic in the samples that would indicate poisoning.

Kentucky's chief medical examiner, Dr. George Nichols, initially contacted ORNL because of the Laboratory's expertise in a technique known as neutron activation analysis (NAA), which can identify trace concentrations of elements.

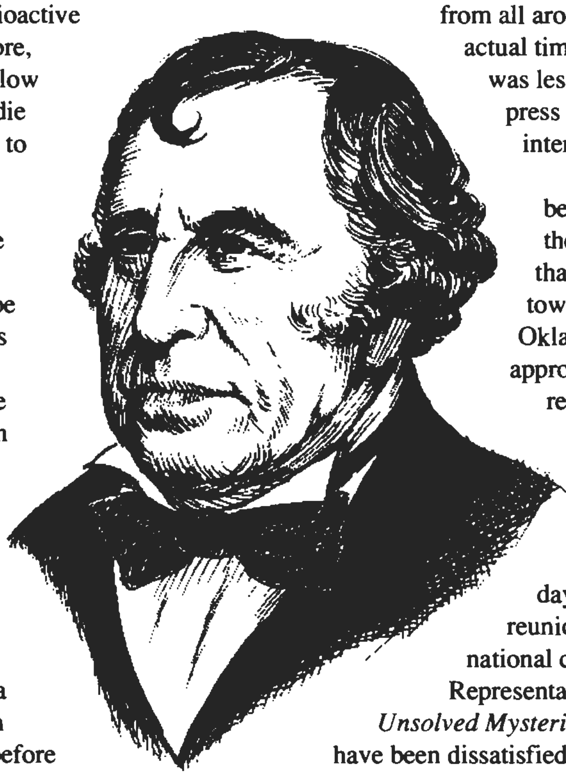
In NAA, a sample is bombarded with neutrons. Atoms in the sample absorb some of the neutrons, becoming heavier, unstable isotopes that emit gamma rays as they decay. Researchers can measure the energies of the gamma rays with a high-resolution gamma spectrometer. Certain energies indicate the presence of certain elements within the original sample.

Dyer and Robinson say that Taylor's remains contain less than 2 parts per million (ppm) of arsenic. A level of 200 ppm or higher would have instigated further investigation. According to Robinson, a massive dose of arsenic can appear in hair roots as quickly as one day after ingestion; Taylor was ill for four days before dying, so any poison would have had plenty of time to appear in his hair.

The samples were flown from Louisville to ORNL in a private plane accompanied by the Kentucky medical team that included Nichols; assistant medical examiner Dr. Tracy Corey; and a senior medical student at the University of Louisville, Mark Fulcher. "We considered this a cooperative project with Nichols and the others from Kentucky," Dyer says. "It was not just an analysis of samples; it was a collaboration."

The samples were irradiated in the HFIR for 1 minute and then counted periodically for 10 hours, until measurements of arsenic levels could be made. Arsenic cannot be measured directly after irradiation because its concentration is too low compared to sodium. A common element in human hair, sodium also becomes radioactive when struck by neutrons, and the gamma-ray emissions from sodium interfere with arsenic readings. However, half of a sample of radioactive sodium will decay in 15 hours, whereas the half-life of radioactive arsenic is 26 hours. Therefore, waiting several days will allow the sodium interference to die away and the arsenic levels to be read.

"The sodium levels are similar to background noise in an office," explains Robinson. "You wouldn't be able to hear someone unless he spoke louder than the noise. In this case, the noise starts off very loud and then becomes softer, until we can 'hear' the arsenic."



The scientists used a new NAA facility at the HFIR to analyze the samples. They were able to achieve better results with a new pneumatic tube system that was installed in 1986 before the HFIR was shut down for three years because of safety and management concerns. When it began to operate in 1990, the new pneumatic tube system enabled researchers to irradiate samples under conditions more advantageous for certain types of materials, such as biological and other delicate materials.

The Taylor investigation brought more national attention to ORNL than the Laboratory has had in a while. Stories appeared in newspapers from the *New York Times* to the *Los Angeles Times*, and the Kentucky press conference revealing the results of the investigation was covered live by the Cable News Network. Robinson, Dyer, and the ORNL Public Affairs office were deluged with phone calls for information. However, the researchers soundly refused to divulge any information, saying it was up to the Kentucky team to evaluate the experiment's results. The morning of that press conference, Nichols' office was broken into by media representatives anxious for the scoop. "If you can imagine people breaking into Nichols' office," Robinson says, "you can imagine the type of intensity that we were getting here from all around the country. The actual time we spent analyzing data was less time than we spent at press conferences and interviews."

Dyer and Robinson became minor heroes during the investigation. Dyer says that residents of his home town, Webbers Falls, Oklahoma (population approximately 400), all remember the local scientist, who was also involved in the Kennedy assassination investigation. Robinson was the celebrity of the day at a recent family reunion in Memphis and at a national convention in Houston. Representatives from NBC's *Unsolved Mysteries* television show may have been dissatisfied with the results of the investigation, but the ORNL researchers were not. (They presented a paper on the NAA analysis at a meeting of the Analytical Chemistry Division in Gatlinburg, Tennessee, in October.) Robinson jokes, "I don't know what would have happened if we had detected a lot of arsenic, but I doubt we would have the time to be sitting here for this interview!"

In the aftermath of all this attention, how do the researchers feel they handled the project? In an understatement, Dyer says, "We lost a little sleep and a little time from other projects." Says Robinson, "I'll have to wait a few months to let it all soak in. It's been fun in a lot of ways, but what was important to us was to do the best work we could with the samples." Zachary Taylor would have appreciated their hard work.

—Alexandra Witze, ORNL Review *summer intern and senior at the Massachusetts Institute of Technology.*

Tower Shielding Facility Test

Some important measurements for a major reactor shielding experiment, conducted jointly by the United States and Japan, have been completed at ORNL's Tower Shielding Facility—the only 1-MW reactor in the world totally dedicated to nuclear shielding experiments. These measurements were the result of completing the first of six experiments planned since the joint program resumed in August 1990.

The measurements were made to determine the effectiveness of geometrically different axial shield designs for liquid-metal–cooled reactor concepts. The data helped researchers compare the abilities of steel and boron carbide materials to protect vessel components from radiation damage.

The experiments' findings should lead to improved designs for shields to protect vessels of the smaller and stronger advanced liquid-metal–cooled reactors expected to be built in the 21st century. Other results may guide the designs of compact, cost-effective shields for liquid-metal–cooled reactor programs in Japan and improved shield designs for existing modular gas-cooled and light-water reactors in the United States and Japan.

New Bioreactor Can Produce Organic Acids

Biodegradable plastics are in demand to reduce the volume of plastic waste disposed in landfills, but because some biodegradable plastics are made from lactic acid produced from expensive petrochemicals, they divert imported oil needed for energy. However, a more economical method of producing such plastics without using oil may be on the horizon.

ORNL researchers have developed a system that uses microorganisms to convert sugar to lactic acid and other organic acids. This innovation for producing organic acids is called a biparticle fluidized-bed bioreactor because it contains two types of particles. They are (1) immobilized microorganisms suspended in liquid that continuously produce useful chemicals and (2) other suspended particles that continuously absorb the product for eventual harvesting.

The microorganisms, also called the biocatalyst, are suspended in the reactor by the upflow of fluid feed materials (e.g., sugar dissolved in water). The other particles, which move through the reactor, are a biological or inorganic absorbent that remove the product of the microorganisms (e.g., lactic acid).

Bioreactor experiments conducted by Brian Davison and Chuck Scott, both of ORNL's Chemical Technology Division, have shown that suspended particles of activated charcoal can continuously remove and concentrate the organic products of the microorganisms, thereby eliminating a reaction inhibitor. The charcoal particles are then removed from the bioreactor, processed to recover the product, and recycled through the bioreactor.

Scott envisions commercial systems consisting of fluidized beds 1.8 to 2.4 m (6 to 8 ft) in diameter and up to 6 m (20 ft) high. "The absorbent would remain in the beds for up to 2 hours before it would enter the chemical recovery phase," he says. "The product could be removed chemically or by a change in the system's temperature. This concept could also be used to convert dissolved sugar to alcohol as well as a variety of organic acids."

ORNL Wins Three R&D 100 Awards

In the fall of 1991, three ORNL developments received R&D 100 Awards from *Research & Development* magazine. The magazine's editors selected these developments to be on their list of the top 100 new technology advances in the world.

The winning entries and researchers were the Direct Braille Slate, which permits blind persons to write from left to right instead of the reverse; a device that uses electromagnetic forces to remove nonmetallic inclusions from liquid metal; and a device for rapidly analyzing the contents of aviation and motor fuels.

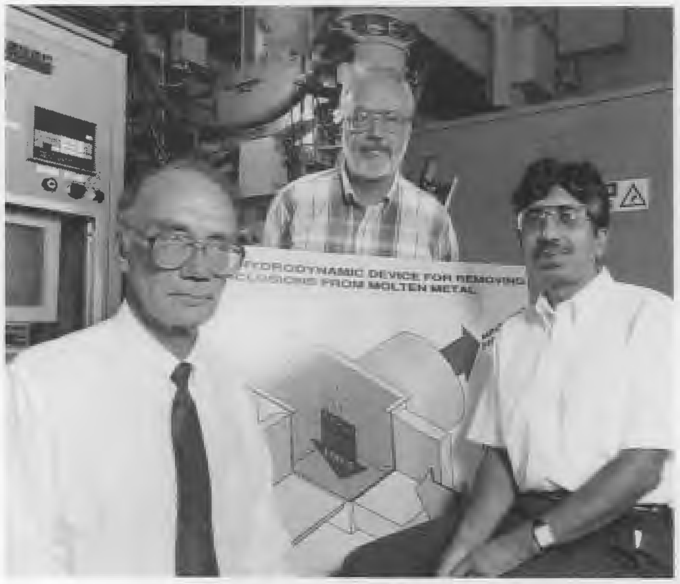
Joe Turner demonstrates the Braille Slate that he and Larry Hawk (right) invented.

Direct Braille Slate. The work of two engineers in ORNL's Applied Technology Division may soon be helping many thousands of handicapped persons throughout the world. Larry Hawk and Joe Turner have invented a mechanical device that enables blind persons to write the Braille alphabet—a system of raised dots that is read by feeling each character—directly from left to right. Their invention is the first improvement in the method of writing Braille since the alphabet was invented in 1824.

Currently, anyone wishing to read and write Braille must learn two different alphabets, backward and forward Braille. The Braille Writer now in use requires the user to punch out each character, from right to left, on the back side of the page. The resulting pattern of dots cannot be read unless the paper is removed from the device and flipped over. As a result, the writer cannot read the characters that have been written until the entire page is completed, which makes drafting original text very difficult.

Using the Direct Braille Slate devised by the ORNL engineers, the writer needs to know only one Braille alphabet and can read the characters while the paper is still in the device. The inventors developed a hand-held hollow stylus that is pushed onto the paper over a bed of vertical pins, leaving a raised dot. As the Braille characters are written, they can be read from left to right.

"The Braille Slate will help the 165,000 blind Americans who can read but not write Braille," Hawk says. "It is estimated that widespread use of the new device may save $85 million in the



Igor Alexeff (left) of the University of Tennessee and David Hobson and Vinod Sikka, both of ORNL, invented the electromagnetic liquid metal inclusion removal device.

Bob Lauf and Barbara Hoffheins devised a rapid fuel analyzer for applications such as detecting hazardous chemical spills.

United States alone because of the reduced time and cost for teaching the estimated 50,000 newly blind persons to write Braille."

Electromagnetic Liquid Metal Inclusion Removal Device. Many metallic components made from steel, aluminum, nickel, titanium, or other alloys can crack when they contain nonmetallic impurities, such as oxides, nitrides, or carbides. To solve this problem, ceramic filters traditionally have been used to remove the solid impurities from the molten metal before it is cast into thin sections and rolled into sheet (for making beverage cans, for example).

Unfortunately, such filters tend to clog and even break, adding unwanted solids to the molten metal. Other impurities are liquid at the melt temperature and, therefore, are not removed by the filters.

These difficulties could be overcome by a new separation device invented at ORNL by Igor Alexeff, an ORNL consultant and professor at the University of Tennessee, and David Hobson and Vinod Sikka, both of ORNL's Metals and Ceramics (M&C) Division. Called the Electromagnetic Liquid Metal Inclusion Removal Device, it uses magnetohydrodynamic forces to remove nonmetallic solid or liquid inclusions from liquid metals. The only requirement is that the inclusions have electrical conductivity or magnetic properties different from those of the melt.

The developers say that the magnetohydrodynamic forces increase the apparent density of the molten metal over that of the inclusions. "By judiciously directing the forces in the proper direction," Hobson says, "the floating inclusions can be caused to migrate to a location where they can be trapped and removed from the molten metal."

Rapid Fuel Analyzer. ORNL researchers have developed a chemical sensor that can recognize seven aviation fuels, determine the presence of chemicals for removing ice (deicer) in aviation fuel, detect ethanol in gasoline, and indicate gasoline's octane rating. No other instrument is known to provide such a rapid and simple classification of so wide a variety of fuels.

The rapid fuel analyzer is less expensive and much faster than conventional analytical instruments, such as mass spectrometers and gas chromatographs. It was developed by Barbara Hoffheins of the I&C Division and Robert Lauf of the M&C Division. (See the additional description of this development in the article "Sensors for Health and Safety" in this issue.)

The developers say that the rapid fuel analyzer could be used by government inspectors to check gasoline at the pump to verify its octane rating and alcohol (ethanol or methanol) content.

"For unleaded gasoline, our instrument can determine the octane rating—whether it be 87, 89, or 92—in approximately five minutes," says Lauf. "The standard tests, which use a single-cylinder engine, can take several hours. An inspector could check 20 to 30 samples by our technique in the time it takes to run one test by the old method."

"It can also be used at airports, marinas, and other refueling facilities to ensure that each vehicle receives the correct type of fuel and to verify the identity of incoming fuel loads."

The rapid fuel analyzer is based on an array of metal oxide gas sensors that react to fuel vapors giving each fuel a distinctive signature. The signatures are the result of the measured electrical resistance of each metal oxide, which decreases in the presence of the target fuel vapors.

Matt Scudiere holds a new, integrated circuit he designed for coordinated data handling in a highly sophisticated portable data acquisition system. This single semiconductor chip has the equivalent circuitry of several hundred conventional integrated circuits, as many as are shown in the stack in front of Scudiere.

The signatures are "learned" by a neural network simulation program called ANSim, which was developed by Science Applications International Corporation. When an unknown fuel is analyzed, the neural network examines the signature and, by comparing it to known fuel signatures, indicates the fuel type it most closely matches.

ORNL Chip Makes Digital Recorder Portable, Practical

An ORNL researcher has developed a new, lightweight, portable system for intelligently recording and playing back data from 100 or more sources. Although this digital recording system was developed two years ago, its combined features still make it "10 to 20 times better" than any data acquisition system on the market.

According to developer Matthew B. Scudiere of the Applied Technology Division, "Our new system records and plays back data at a higher speed and

"Use of this chip reduces the weight and size of the recording system enough to make it both practical and portable."

with greater accuracy, and it handles a higher volume of data arriving along many different paths at different speeds." Unlike other systems on the market, Scudiere's system, called TERADAC, can operate at high speed and handle large volumes of data at the same time.

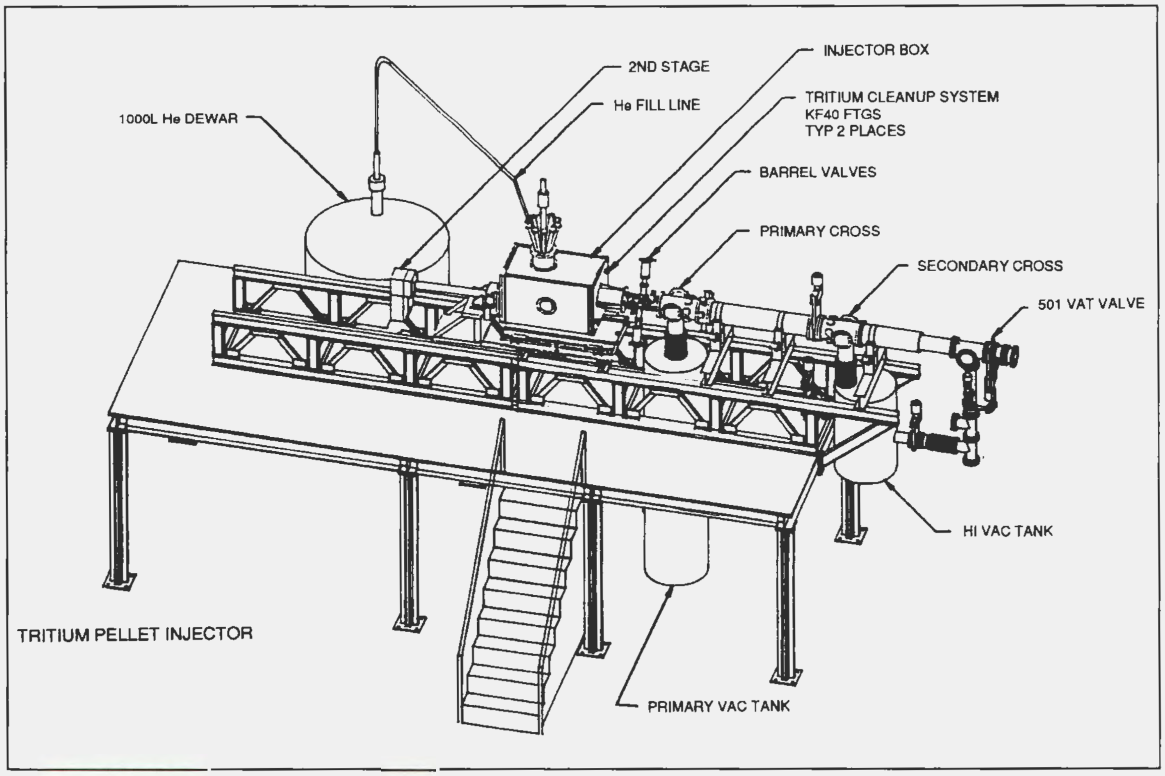
The heart of TERADAC is an applications specific integrated circuit (ASIC) designed by Scudiere. "Use of this chip," he says, "reduces the weight and size of the recording system enough to make it both practical and portable.

"If the circuit on our ASIC chip were implemented using conventional integrated circuits, 300 to 500 chips on a board about 20 inches square would be required, making the system too large to be practical. This chip was designed to be a universal interface between our system and most of the analog-to-digital converters on the market as well as a controller for the various devices that connect to the system."

This sophisticated data acquisition and control system was developed to record high-resolution sonar phased array signals—sound waves from many different microphones that could be used, for example, to construct a map of the undersea terrain showing the locations of rocks, mines, and submerged ocean vessels. It also records lower-speed signals of interest, such as those from factories, control processes, and test craft, all of which have a large number of variables to monitor.

This flexible system can accept data in a variety of forms, including digital inputs, direct-current voltages, acoustic signals, and video signals. It can record 48,000 megabytes of data per hour at a cost of less than $2 per megabyte, and it allows data to be stored at a cost of less than 0.2 cents per megabyte. The system can record data at full bandwidth of 12.8 megabytes per second for a full hour or for proportionally longer times for slower recording rates.

TERADAC consists of a central computer, a rugged digital recorder, and a rack system for a



This drawing shows a 3-D model of a tritium pellet injector designed at ORNL.

host of various data modules, each containing an ASIC.

New Uses for ORNL's Pellet Technology

The pellet propulsion technology developed at ORNL in the 1980s for refueling experimental fusion devices is now being adapted for other applications.

The technology of shooting pea-size cylindrical pellets at a target has been studied as a possible substitute for sandblasting for removing contaminants (including metal oxides) from metal and concrete surfaces. It is being considered for removing paint and simulating the effects of flying space debris on the proposed U. S. space station.

Pellet fueling of experimental fusion devices—a technology supported for nearly 20 years by DOE's Office of Fusion Energy—continues to be a major mission of ORNL's Fusion Energy Division. It will be a large contributing factor in the achievement of energy break-even (energy output equals energy input) in the mid-1990s.

Pellet-accelerating devices developed under the leadership of Stan Milora and Chris Foster, both of the Fusion Energy Division, are currently operating on three experimental doughnut-shaped fusion devices called tokamaks. They are the Joint European Torus (JET) in England, the Tore Supra in France, and the Tokamak Fusion Test Reactor (TFTR) in Princeton, New Jersey.

Milora, program manager for Fusion Plasma Technologies at ORNL and leader of his division's Plasma Fueling Group, said that both the JET and TFTR will achieve energy break-even between 1993 and 1995 when they switch their fuel from deuterium to deuterium-tritium (a mixture of two heavy hydrogen isotopes). "Both tokamaks," he said, "are close to achieving the conditions that would lead to energy break-even if they replace deuterium with tritium." With DOE funding, the ORNL group is currently building a tritium-pellet injector for the TFTR (see figure at left).

The injectors propel pellets of frozen deuterium into the center of the tokamak's hot, ionized deuterium plasma, which is confined by magnetic fields within the fusion vessel. The pellets increase the plasma density, helping to sustain the fusion reactions needed to provide the heat energy required to produce electricity. Milora says that the pellet injector at the JET has helped this machine raise its product of energy confinement time, plasma temperature, and plasma density by a factor of 10.

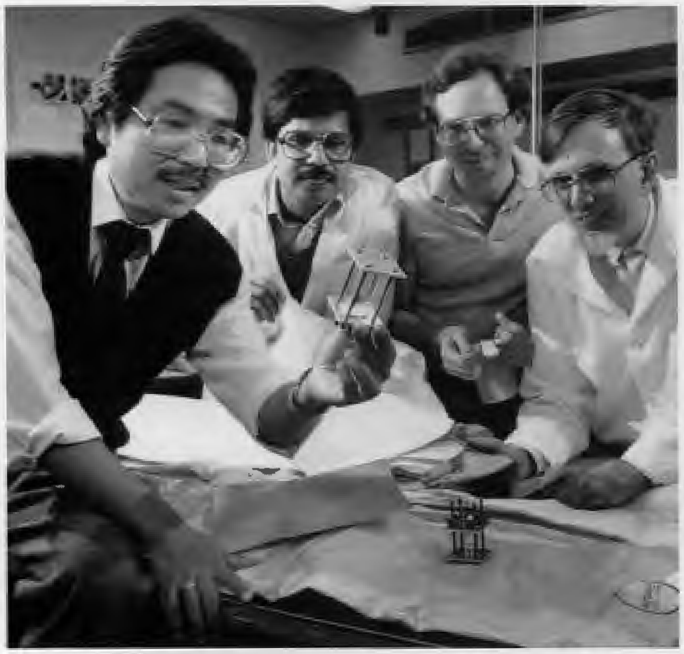
Milora is in charge of the fusion applications of pellet injection, and Hal Haselton heads the nonfusion applications of this technology. Pellet acceleration of cryogenic materials has been considered as a replacement for sandblasting to remove contaminants from concrete and metal surfaces. The problem with sandblasting is that it produces a sizeable waste stream consisting of water, sand, and the waste material that must be removed for disposal. Pellets of carbon dioxide (dry ice) or argon ice do not produce waste streams because they evaporate into the air, releasing inert gases. The mixed contamination liberated in the process would be pulled from the air by high-efficiency particulate absorbant filters.

"ORNL is also proposing the use of pellet technology to simulate the results of collisions expected between meteorites and space debris and the proposed U. S. space station."

ORNL is also proposing the use of pellet technology to simulate the results of the collisions expected between meteorites and space debris and the proposed U. S. space station, to be orbited later this decade by the National Aeronautics and Space Administration (NASA). Two kinds of debris would be simulated—flying debris that collides head-on with the moving space station and "tail chasers" that strike the spacecraft from behind.

The centrifugal pellet injector designed under Foster's leadership for the Tore Supra was used in the first demonstration of pellet fueling in combination with "lower-hybrid radiofrequency power." The centrifugal injector uses a high-speed wheel to accelerate frozen pellets of deuterium and inject them into the plasma center.

Milora and Steve Combs have developed another type of injector that is similar to a BB



Tuan Vo-Dinh examines a glass permeation cell used to measure the rate of permeation of chemical agent simulant through protective clothing. Co-investigators are, from left, Tarasankar Pal, Gordon Miller, and Guy Griffin.

gun. They have built several one-stage light-gas guns and are building a two-stage gun.

In a single-stage gas gun, frozen pellets of deuterium are cut one at a time from extruded deuterium (just as cookies are cut from dough squeezed from a tube). Each time a pellet forms in the gun barrel, a valve opens and hydrogen gas rushes in, propelling each pellet through the barrel and into the fusion device vessel. ORNL's three single-stage gas guns on the JET force pellets of up to 6 mm in diameter into the plasma at a speed of 1.3 km/s. These injectors, which have been used for experiments on the JET since September 1987, will complete their mission in January 1992.

To increase the pellet injection speed 3 to 5 times, Combs, Mike Gouge, and Charles Foust are building a two-stage gas injector. In this system, the force of the hydrogen propellant is greatly increased by compressing it with a titanium piston. Compression raises the hydrogen pressure to 50,000 psi and the temperature to 10,000°C.

ORNL's single-stage gas gun that had operated on the TFTR since 1986 was returned to the Laboratory in July 1991. This machine will be upgraded into a two-stage gun that can propel frozen pellets of tritium. The new tritium injector will be used by the TFTR when it starts operations with a deuterium-tritium plasma in July 1993.

New Chemical Protection Suit Test Devised

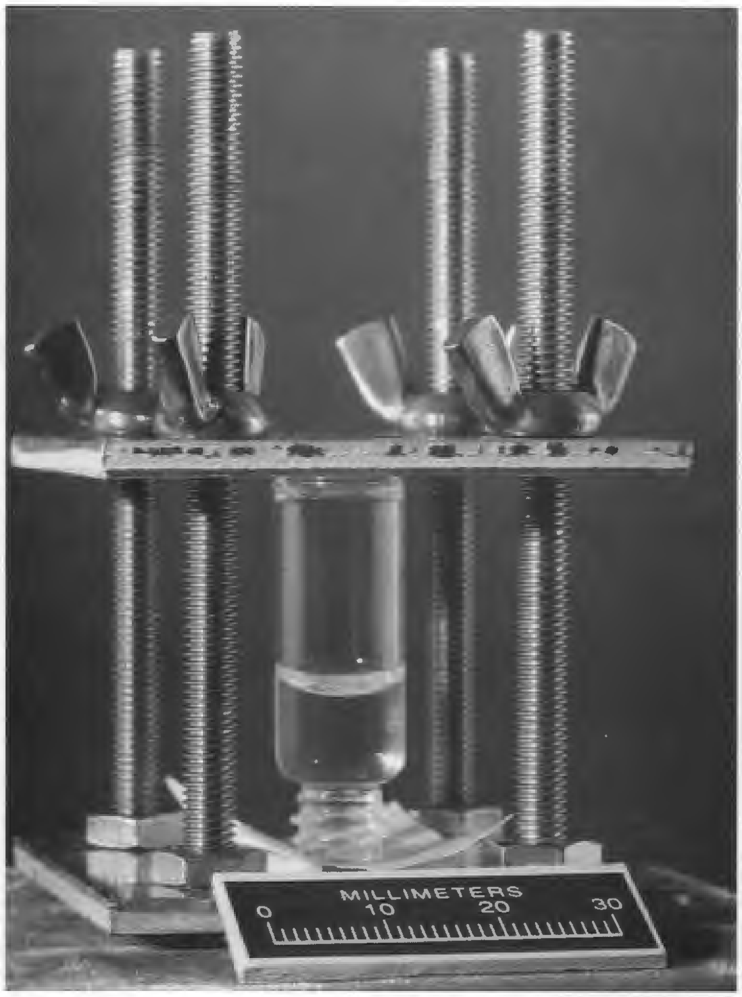
ORNL researchers have developed a new technique that could help the Federal Emergency Management Agency (FEMA) select the types of protective clothing materials that offer the best protection against chemical warfare agents for civilian emergency workers. This project is part of a larger activity providing technical support for reentry decision making in the joint Army-FEMA Chemical Stockpile Emergency Preparedness Program (CSEPP).

The findings could guide FEMA in choosing chemical protection suits for emergency personnel responding to possible off-site contamination by unitary chemical warfare agents. Munitions containing undiluted nerve or blister agents are undergoing destruction, as required by law and proposed in international arms control treaties.

Such suits will be needed for civilian emergency operations and by civilian emergency personnel dealing with any unplanned releases of chemical warfare agents from stockpiles at eight U. S. munitions storage sites. The findings are also of interest to civilian emergency planners preparing for future conflicts similar to the Persian Gulf War, in which Israeli and Saudi communities had to face the possibility of a chemical weapons attack.

"Because of the possibility that chemical warfare agents could pass through commercially available 'hazmat' suits and enter workers' bodies through the skin, we developed a simple analytical technique for determining how long various protective clothing materials could actually shield personnel from these lethal agents," said Tuan Vo-Dinh, leader of the Advanced Monitoring Development Group in ORNL's Health and Safety Research Division (HASRD). "In the case of one type of chemical warfare agent simulant, we found that the time of protection for various materials ranged from as long as 24 hours to as short as 10 minutes."

A new technique developed by Vo-Dinh and Tarasankar Pal, also of the Advanced Monitoring Development Group, detects and measures the permeation of chemical warfare agent simulants through protective suit and glove swatches. The experimenters used simulants because they are chemically similar to, but much less toxic than, the warfare agents that the U. S. Department of the Army plans to destroy by 1999.



In chemical protection suit studies, a swatch of protective clothing material is placed at the open end of a glass permeation cell containing a chemical agent simulant. Positioned over this swatch is a disk of filter paper treated with an indicator compound. The glass cell is inverted, and gravity forces the chemical agent to "challenge" the surface of the protective clothing sample.

Exposure to high concentrations of organophosphate nerve agents such as VX and GB can be lethal in minutes. These odorless, colorless chemicals interfere with the normal function of the nervous system and can be absorbed through the skin of an unprotected person or inhaled. Sulfur mustard and other blister agents that are inhaled or come in contact with the skin can cause eye and skin irritation, temporary blindness, blisters, vomiting and nausea, and respiratory difficulties that can be fatal.

As a result of the experimental measurements, Vo-Dinh and his colleagues found that a GB nerve agent simulant passes through a swatch of a widely used protective material (a laminate of nylon and polyvinyl chloride) in only 10 minutes—the "breakthrough time." They determined that the most effective chemical protection material against this simulant consists of laminated materials having butyl or teflon coatings; their breakthrough time was more than 24 hours.

Some of these findings were obtained in late 1990 during the presence of U. S. military forces in Saudi Arabia. Because of the possibility that civilians would have to protect themselves against chemical weapons attacks by Iraqi forces, the ORNL research team received inquiries from planners associated with Operations Desert Shield and Desert Storm.

To measure the diffusion of a nerve gas simulant through protective-clothing swatches, Vo-Dinh and his colleagues developed a "spectrochemical modification" technique using a glass cell, xenon arc lamps, and two photometric detectors that measure the intensity of light emissions.

"This is the first time," said Vo-Dinh, "that this spectrochemical modification technique has been used for detecting the permeation of chemical warfare agent simulants through chemical protective clothing."

In a typical experiment, a swatch of protective clothing material is placed at the open end of a glass permeation cell containing a small amount of chemical agent simulant. Positioned over this swatch is a disk of filter paper treated with phenanthrene, an indicator compound. The glass cell is inverted, and gravity forces the chemical agent to "challenge" the surface of the protective clothing sample.

If any of the simulant permeates the protective clothing swatch, it is absorbed by the treated filter-paper disk. After a measured exposure time, the filter-paper disk is removed and analyzed to determine the amount of chemical agent simulant present, if any. The analysis is based on spectrochemical modification—changes in the intensity of emitted light.

When a xenon lamp shines light of a specific frequency on the filter-paper disk, the electrons in the indicator compound are excited, resulting in the emission of light. The intensity of this luminescence, which is measured by a photometric detector, is constant if the filter paper contains only the indicator compound.

However, if a chemical agent simulant is taken up by the filter-paper, the simulant will modify some of the light emitted by the excited indicator compound, thus changing the intensity of its luminescence. The weaker the light signal detected, the greater the quantity of chemical agent simulant in the filter paper disk.

"Detection of spectrochemical modification, or quenching of the phenanthrene's luminescence," said Vo-Dinh, "indicates that the chemical agent simulant passed through the protective clothing. Measuring this effect allows us to determine the breakthrough time with great sensitivity."

Other participants in the project were HASRD researchers Mary Lou Daugherty, Guy Griffin, Gordon Miller, and Annetta Watson. Watson is task leader of Reentry Technical Support for ORNL's CSEPP Team, which includes investigators from HASRD and the Analytical Chemistry, Energy, and Environmental Sciences divisions.

A Look at Yellowstone's Post-Fire Landscape

The summer of 1988 was the driest in recorded history for Yellowstone National Park. By August, the park was receiving only 10% of its normal precipitation. When lightning struck, the lack of rain and the high winds helped ignite the largest fires ever experienced in a national park in the continental United States. The effects on the park's ecosystem may not be known for many years, but researchers are already identifying early impacts and signs of recovery.

Monica Turner and Bob Gardner, both of ORNL's Environmental Sciences Division, are working with Bill Romme of Fort Lewis College to characterize the ecological effects of large-scale fires on Yellowstone. Along with ORNL postdoctoral research associates Bill Hargrove, Scott Pearson, and Yegang Wu, they are studying the extreme patchiness of the post-fire landscape. Understanding the causes and consequences of this diverse landscape is important for managing park resources and for overall understanding of landscape ecology.

In 1989 Turner and her colleagues established three study plots in Yellowstone, each a 1-km^2 grid containing 100 sampling points. At each point they measured characteristics such as burn severity, plant species present, density of trees, depth of ash and charred soil, and percentage of vegetation cover. Over several years, they developed from these data several hypotheses on the regeneration of plants following a large-scale fire.

Members of a crew that included ORNL researchers take samples in a burned forest at Yellowstone National Park.

Plants with different modes of reproduction expand into burned areas differently because of the ways in which they regenerate. For example, Turner says, "One response might be that the plant simply resprouts from its surviving plant parts, or rhizomes, below the charred soil. In that case we hypothesize that the size and shape of the burned patch aren't really going to matter, because the placement of the rhizomes is unaffected by the fire."

Other plants reproduce by aerial spread of seeds. A well-known example is the lodgepole pine, whose cones are stimulated by fire to release their seeds. The dispersal of seeds into a burned area may depend on wind conditions or transport by water or animals. In this case the regrowth may be influenced by the size and shape of a burned patch, because the airborne seeds may not be able to reach all parts of a large area.

Why is it important to understand the regrowth of vegetation after a large fire? "This will tell us the importance of a patchy distribution of habitat types—what we call landscape heterogeneity—to the ecological processes of an area," explains Turner. Her work focuses on the role of natural disturbances, such as fires, in an ecosystem. She adds, "We hope that our work will give further insight into the interactions between vegetation patterns and ecological processes in all landscapes."

Turner and her colleagues are also trying to determine why the fires burned in such an

"The effects on the park's ecosystem may not be known for many years, but researchers are already identifying early impacts and signs of recovery."

The mosaic of burned and unburned forest in the Yellowstone landscape is a subject of ORNL research.

unusually patchy pattern. The severe fires occurred most frequently in older forest stands (over 300 years old).

"In Yellowstone, the flammability of the forest increases with age," Turner explains. "The older stands have old, tall trees as well as younger trees that are growing, so there is a continuous canopy of branches and leaves that can burn. In contrast, the younger forests tend not to have much understory, and the fire can't get from the forest floor to the canopy as easily."

Before 1988, fires observed in Yellowstone burned only in the older stands, as expected. However, the summer of 1988 was so dry and windy that the younger stands began to burn in August and September. Turner and her associates believe that pre-fire landscape and weather conditions have interacting roles in controlling fire, possibly explaining the patchy burning pattern.

"If you have a summer that's normally dry, then we think that the landscape pattern of older stands controls the severity and spread of the fire. But if you have an extremely dry summer, which occurs around every two centuries, then the landscape pattern probably doesn't matter, because it's simply the weather that controls what happens."

A second Yellowstone project was initiated in 1990 to study the relationships among the fires, revegetation, and the survival of elk and bison in the park. Turner, Romme, Wu, and Linda Wallace of the University of Oklahoma are investigating the effects of fire scale and severity on the survival of the elk and bison and on the regeneration of the food plants preferred by the animals.

The animals spend the winter in the northern range of Yellowstone, and their survival depends on the forage available during that harsh season. Generally speaking, in the first post-fire year, no food is available in burned areas because plants have not yet had the chance to regenerate. From the second year on, plants begin to flourish in burned patches, and forage in these areas tends to be more lush and nutritious.

The scientists are observing the behavior of the animals, and they believe that differences in fire scale and heterogeneity will affect the elk and bison differently because of the changes in the quality and quantity of food available after the fire. They are working on a computer simulation to predict plant and animal dynamics under varying fire, weather, and population conditions. They will eventually compare their predictions with field observations to determine if they are accurate.

The researchers found several surprises during their study, including the unexplained appearance of aspen seedlings in a burned area previously dominated by the lodgepole pine. They will be busy for several years trying to explain these findings and conducting their planned research. Despite the destruction they caused, the extensive 1988 fires of Yellowstone will be remembered for one fortunate reason—a rare chance to study the national park's dynamic landscape.

Energy Systems Enters 11 CRADAs in a Year

On August 15, 1990, Energy Systems became the first DOE management contractor to receive authority to implement CRADAs—cooperative research and development agreements established by the National Competitiveness Technology Transfer Act of 1989. By August 12, 1991, almost a year later, Energy Systems had signed 11 CRADAs with various industrial firms.

A CRADA is a joint venture between the DOE contractor and industry and provides a means for contractors to share capabilities, facilities, and technologies available at DOE facilities with U.S. industry, universities, and other research and development (R&D) organizations. Costs are also shared. The purpose of CRADAs is to improve U.S. competitiveness in the world marketplace.

Ozone-safe chemicals. In 1990 Energy Systems signed its first CRADA with an international consortium called the Alternative Fluorocarbons Environmental Acceptability Study (AFEAS). This consortium is funded by 12 chemical producers from several countries. The CRADA enables AFEAS to work with ORNL to study the potential environmental, health, and safety effects of chemicals proposed as alternatives to chlorofluorocarbons to protect the stratospheric ozone layer that protects humans from damaging ultraviolet radiation from the sun. (For details, see "Technology Transfer" in the Vol. 24, No. 1, 1991, issue of the *Review*.)

Help for state industry. In June 1991 Energy Systems entered into two CRADAs with the state of Tennessee to help Tennessee firms implement environmentally sound manufacturing processes and improved metalworking and machining operations. The agreements pledged regional technical assistance and cooperative R&D. (For

Energy Systems and GE entered into a CRADA in August 1991 to find ways to use bacteria to treat toxic PCBs. Participating in the CRADA signing ceremony were, from left, Clyde Frank, DOE's Office of Environmental Restoration and Waste Management; Samuel Schulhof, GE's Environmental Research Center; ORNL Director Alvin Trivelpiece, and Warren Siemens, Energy Systems.

details, see "Technology Transfer" in the Vol. 24, No. 2, 1991, issue of the *Review*.)

Taking advantage of the materials expertise in ORNL's Metals and Ceramics (M&C) Division, Energy Systems entered into five more CRADAs by the middle of 1991. Other CRADAs involved researchers from the Energy and Chemical Technology divisions.

Shape-memory alloys. One CRADA, which uses ORNL's expertise in developing ductile nickel aluminide alloys, was signed with Eaton Corporation and Johnson Controls, Inc. Its purpose is to develop a shape-memory alloy that retains its shape even at high temperatures.

Under this agreement, ORNL would design, develop, and characterize nickel aluminide alloys as high-temperature shape-memory materials for control systems. A goal of the work is to develop more ductile materials that maintain their shape-memory capability at or above 150°C. Eaton and Johnson Controls will evaluate and optimize the shape-memory effect and will test materials and parts.

Microwave annealing of silicon nitride. Three CRADAs involving the M&C Division make use of ORNL's microwave furnaces to improve the strength and toughness of ceramic components for use in energy-efficient high-temperature engines. As part of the agreement, ORNL scientists at the High Temperature Materials Laboratory will conduct collaborative research on silicon nitride with staff from Garrett Ceramic Components of Torrance, California, a division of Allied-Signal Aerospace Company, and the Norton Company's Advanced Ceramics Division of Northboro, Massachusetts.

The cooperative work will investigate the ability of microwaves to alter the microstructures of dense pieces of silicon nitride so as to improve their properties. Garrett will test microwave-annealed compositions that are high in additives (>5 wt %), and Norton will test low-additive compositions.

ORNL experiments have shown that, when heated by microwaves, beta silicon nitride grains making up the ceramic's microstructure can grow into whisker-like shapes that improve its toughness and high-temperature creep resistance, making it less brittle. Silicon nitride and other ceramics are preferable to metals for engine components because they are lighter, more durable, and able to withstand much higher engine temperatures, which would make possible a 25% increase in fuel-use efficiency.

Mark Reeves of ORNL's Chemical Technology Division will work with the General Electric Company under a CRADA devoted to developing biological treatments of soils contaminated with PCBs. Here, he adds PCB-free soil to anaerobic, bench-scale bioreactors.

The two companies will provide dense silicon nitride specimens of three proprietary compositions to ORNL, and ORNL researchers will test the ability of industrial-size microwave furnaces to anneal test shapes of this material to alter their microstructures. The companies will use conventional annealing on specimens of the same composition, and all parties will determine and compare the physical and mechanical properties of all test shapes. The expected result of this effort is a demonstrated microwave technology for fabricating toughened heat-engine

Warren Siemens (left), deputy director of Energy Systems' Office of Technology Transfer (OTT), and Maxine Savitz, director of Garrett Ceramic Components, signed a cooperative research and development agreement (CRADA) July 16 in a ceremony at ORNL's High Temperature Materials Laboratory. Watching is Sylvester Scott of OTT. Through the CRADA, the ceramics company will have direct access to ORNL equipment and expertise for evaluating microwave processing for making tougher ceramic components for engines.

components at a cost lower than that of conventional annealing.

Attic insulation tests. In May 1991 Energy Systems entered into a CRADA with an association of companies in the Cellulose Industry Standards Enforcement Program (CISEP). The purpose of the agreement is to jointly evaluate the resistance to heat flow in a conventional attic of blown cellulose insulation having various densities.

All tests are being performed at DOE's Roof Research Center at ORNL. CISEP provides blown cellulose insulation of various densities. ORNL researchers conduct tests to determine the ability of each insulation to prevent convective heat losses (those resulting from the natural circulation of air) that may be induced by temperature differences in the attic. The results of these tests will guide CISEP in determining the most effective insulations and will help DOE develop criteria for more energy-efficient buildings.

Two CRADAs with refrigerator manufacturers. In July 1991 Energy Systems signed two CRADAs with the Appliance Research Consortium (ARC). The goal of one CRADA is to conduct a series of tests to aid in the design and development of home refrigerator-freezers that would use 40 to 50% less electricity than those in use today. The goal of the second CRADA is to develop a lifetime test procedure for powder-filled evacuated panels (PEP), a superinsulation whose resistance to heat flow is 2.5 times that of insulation currently used in refrigerators.

ARC, which is a subsidiary of the Association of Home Appliance Manufacturers, will provide hardware to ORNL, such as heat exchangers, compressors, cabinets, and controls, for refrigerator tests as well as the PEPs for the lifetime test. ORNL researchers in the Energy Division will test various energy-saving concepts (including alternative refrigerants) and publish the results.

Researchers from the M&C Division will develop an accelerated lifetime test for the PEPs that will predict in less than 6 months the thermal resistivity of the PEPs after 20 years of exposure to air. Each ARC member will conduct this procedure to evaluate its precision and bias.

Biodegradation of PCBs. In August 1991, Energy Systems signed a CRADA with General Electric Company to develop effective ways to use microorganisms to break down polychlorinated biphenyls (PCBs). PCBs are toxic materials released to the environment from manufacturing processes, discarded electrical equipment, and other sources.

Both GE and Energy Systems have conducted research on the biodegradation of PCBs because they are searching for effective methods for remediating PCB-contaminated soils and sediments at their facilities. The goal of the CRADA is to accelerate the development and testing of new technologies for the biodegradation of PCBs to meet cleanup standards as low as 2 parts per million in solid matrices.

Electrical engineer Hal Kimrey (left), designer of ORNL's 12-kW microwave furnace shown here, and ceramic engineer Mark Janney examine a silicon carbide ceramic tube that has been heated by microwaves to 1200°C in 5 min.

ORNL researchers are responsible for conducting bench-scale bioreactor tests that will lead to field tests at PCB-contaminated sites on the Oak Ridge Reservation. GE researchers will provide bacterial cultures for these tests and assist ORNL researchers in designing the tests and analyzing treated samples. Energy Systems will provide bacterial cultures for testing in Oak Ridge and at GE facilities, as well as systems and engineering support to GE for field tests to be done at GE facilities.

ORNL Transfers Control Technology to Nuclear Industry

ORNL was recently responsible for the first transfer of advanced digital control technology from DOE's Advanced Controls Program to the American nuclear power industry. ORNL researchers played a key role in developing a significantly improved method of automatically controlling U. S. nuclear power plants.

In 1990 the Reactor Systems Section of ORNL's Instrumentation and Controls (I&C) Division participated in a planned upgrade of the control systems of seven operating nuclear power plants built by Babcock and Wilcox (B&W). A prototype control system will be tested on a power plant simulator in 1992, and the advanced control system will begin operation in at least one B&W plant in 1995.

Because of the unique capabilities of the section's Advanced Controls Program for designing and simulating control systems, I&C researchers Ron Battle, Roger Kisner, Carlos March-Leuba, and Tom Wilson were asked to develop and evaluate conceptual designs to automate operation of the B&W plants. The request was made by the B&W Owners Group, and a work-for-others contract was signed with the I&C section, thus providing a mechanism for the transfer of the ORNL technology to the commercial nuclear power industry.

The B&W group described the plant operation and specified the tasks it wanted the control system to perform. The ORNL group, working at the Laboratory with Bob Winks of B&W, designed control algorithms and tested them in a computer simulation. Several algorithms were developed and compared in a competitive evaluation. (An algorithm is a set of well-defined rules to follow and steps to take to solve a problem; in this case, it is incorporated in a

"ORNL researchers played a key role in developing a significantly improved method of automatically controlling U. S. nuclear power plants."

Carlos March-Leuba (left), Ron Battle, and Roger Kisner (along with Calvin and Hobbes and Bart Simpson on the wall) listen to Tom Wilson making a point about an algorithm they developed for the advanced digital control system of Babcock and Wilcox nuclear reactors.

computer simulation of the B&W nuclear plant.). The goal was to find the best way to improve the B&W reactors' steady-state and transient performance. (A transient is a temporary deviation from the normal, or steady-state, operating condition of the power plant.) Another goal of the ORNL algorithms was to replace operations currently performed manually by the operator with automatic digital control functions, thus freeing operators for higher-level diagnostic and supervisory activities.

"An automatic control system will reduce stress on the operator and equipment," Wilson said. "It will also reduce the number of trips, or interruptions in reactor operation, that result from poor manual operation, making the reactors available for power production for more of the time."

Once the algorithms were developed, the B&W group asked ORNL to test them on 200 simulated transients specified by the group. The algorithms passed all tests.

The new control system has several new features, including fully automatic operation from 1 to 100% power, automatic startup and shutdown of the turbine generator and feedwater pumps, and priority error assignment.

"Priority error assignment," says Wilson, "is a really new control strategy for power plants. The goal is to assign control of the most important errors to systems available to respond. Systems become unavailable, for example, when the operator places them in manual control. Priority error assignment ensures that the parameters most likely to cause a reactor trip are always under control."

As a result of the ORNL effort, Wilson said, the B&W plants in the United States will have a more comprehensive advanced control system than reactors manufactured by other vendors. "The B&W advanced control system," he added, "will integrate the reactor system, the steam system (including the turbine and turbine bypass), and the feedwater system. In B&W reactors, these systems are highly coupled, providing an advantage for the new control system. The systems use a common power set point to balance energy production and heat removal and to help each other control reactor temperature and pressure. The advanced digital control systems developed for General Electric and Westinghouse Electric reactors focus on only the feedwater system."

Operators controlling reactors today read meters, push buttons, and turn knobs, Wilson said, but in a few years, they will be controlling the reactor by viewing video displays and entering commands using a computer keyboard and mouse. The new B&W control system will allow operators to view reactor operations and parameters on "user-friendly" video displays, which will communicate more information to the operator through icons and graphs than through tables of numbers. For example, such video screens will display changes in the temperature and pressure of the reactor coolant almost instantly using brightly colored bar graphs.

"This technology transfer project was a major success for several reasons," said Wilson. "It was a well-defined project that had the support of the Advanced Controls Program at ORNL. The staff of ORNL met regularly with members of the utility operating and engineering staffs. We worked in a competitive design environment in which everyone suggested and evaluated ideas and only the best ideas survived."

A Successful Consortium

ORNL recently played an important role in the organization of what is being considered a highly successful consortium involving university, national laboratory, and industry personnel. As a result, user-friendly software is commercially available and is expected to yield considerable cost savings for industrial firms using refractory materials.

Refractories—clay bricks and other materials that can withstand very high temperatures—are used to make linings for steel blast furnaces, coal gasifiers, and oil refinery vessels as well as ladles for removing steel from furnaces. However, corrosion and various stresses eventually cause these materials to deform and crack so that they must be replaced.

In the late 1970s, because of its interest in the fate of materials in harsh coal-combustion environments, DOE began supporting studies to understand thermomechanical degradation of refractory materials and to develop a computer model to predict when materials used singly or in combination in high-temperature environments are likely to fail.

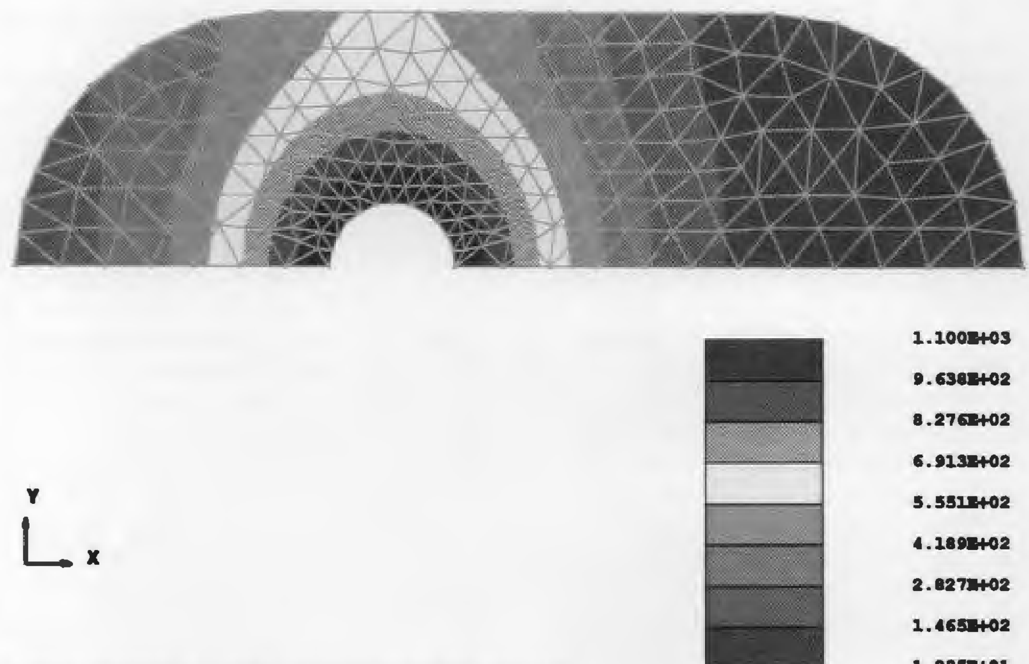
Such a model could help design engineers determine the designs that increase the durability of components made of layers of refractory materials. It could also indicate to plant operators when refractory components most likely need to be replaced.

The ORNL-managed Fossil Energy Advanced Research and Technology Development Program began work at the Massachusetts Institute of Technology (MIT) on developing software to accurately predict the thermal and physical behavior of refractory linings. MIT researchers developed a finite element analysis model for the thermomechanical degradation of refractories.

"This model quite successfully predicted the behavior of refractories under different conditions," says Rod Judkins, manager of ORNL's Fossil Energy Program, "but was fairly difficult to use and required expertise not usually possessed by plant operation and design engineers."

Ron Bradley, then manager of ORNL's Fossil Energy Program, and Oral Buyukozturk, the MIT principal investigator on the project, conceived the idea of developing an intelligent user-friendly software that could be used by design engineers in the field. Bradley suggested that, because this development would be of interest to some industrial organizations, they might be willing to financially support it.

In February 1987, Judkins, then manager of ORNL's Fossil Energy Materials Program, and Warren Siemens of Energy Systems' Office of Technology Applications (now Office of Technology Transfer) organized a meeting at MIT. There they suggested that ORNL and interested private companies form a partnership to develop a user-friendly thermomechanical model. As a result, 12 industrial organizations, including 6 foreign ones, committed 60% of the funding for the work; the domestic companies included Amoco, Combustion Engineering, LTV Steel, Norton Company, and Texaco. The other 40% of the funding was provided by DOE's



Stress contour of a steel component as predicted by thermomechanical software developed through a local consortium.

"Very few software projects of this complexity stay on schedule and within budget as did this one."

Fossil Energy Advanced Research and Technology Development Program.

The partnership was formed under the umbrella of the Thermomechanical Model Software Development Center, a nonprofit organization whose function was to ensure the development of the software. Thus began the evolution of one of the few successful consortia in the United States, according to Siemens. Once operated at Corridor Park on Pellissippi Parkway—the route linking Oak Ridge with Knoxville—this consortium was managed by the Tennessee Center for Research and Development (TCRD), which is supported by the University of Tennessee, the Tennessee Valley Authority, Martin Marietta Energy Systems, and the state of Tennessee.

According to TCRD President Al von der Esch, "We are very pleased with this success for several reasons. It was one of the first of its type managed by TCRD and a textbook example of what we hope to do many times over. The acceptance and satisfaction voiced by all those involved was very gratifying and verified that consortia such as this can work."

Working as a private consultant, John Reed of ORNL's Energy Division provided the leadership to keep the project in focus, on schedule, and within budget. "Very few software projects of this complexity stay on schedule and within budget as did this one," Reed says. "Part of its success was due to the work of bright young engineers, such as En-Sheng Chen of Integrated Engineering Design, Inc., the Houston company formed by Buyukozturk to commercialize the software."

The user-friendly software, called IDEAL, was developed in two years. Today two copyrighted software products produced by the Thermomechanical Model Software Development Center are available for use on SUN and DEC workstations.

Two unexpected spin-offs have resulted from the consortium's development. One company is now using the software to design refractory materials at the molecular level to make them more durable. Another company is using it to train workers to operate oil refineries more efficiently. "Neither use," says Reed, "was envisioned by the authors of the software."

The software is expected to save companies money because they will not have to shut down their furnaces, boilers, refinery vessels, and other operations so often to determine if refractory linings are failing. "It costs an oil refinery $1.5 million a day in lost product each time it must shut down to check on or replace a lining," Reed says. "Thus, the use of the software should reduce downtime and produce significant savings."

"Most consortia fail," says Siemens. "But this consortium with its limited life and limited objective was a success, even without the benefit of CRADAs—the new cooperative research and development agreements that facilitate collaboration between government and industrial organizations." —*Carolyn Krause.*

INDEX OF *REVIEW* ARTICLES TO DATE

(Previous index appeared in Number One, 1984 issue)

Number Two, 1986	State of the Laboratory—1985: How Service Groups Support Research	Herman Postma
	Superconducting Magnets for Fusion Energy: The Story Behind the Six Coils	Paul Haubenreich et al
Number Three, 1986	This special issue on the physical sciences at ORNL covers surface modification, alloy design, materials theory, improved ceramics, irradiation of materials, robotics research, high-energy atomic physics, bioelectronic materials, separation science, water and coal chemistry, mass spectrometry research, and nuclear physics experiments and theory.	
Number Four, 1986	Sizing Up Contaminated Properties: A Saga of ORNL's Western Pioneers	Craig Little et al.
	Genetic Risks of Using Ethylene Oxide	Walderico Generoso
	Human Gene Therapy: A Look at a Cutting Edge of Biomedical Science	Frances Sharples
	Survey Sampling: A Useful Tool for Scientific Investigation	Tommy Wright
	Nuclear Sleuthing at ORNL: A New Look at Neutron Activation Analysis	Carolyn Krause
	The U.S.–Japan Collaboration on Breeder Fuel Reprocessing: ORNL's Role	William D. Burch
Number One, 1987	National Laboratories and Science Education: The University Relations Program at ORNL	Vivian Baylor
	ORNL Follows the Chernobyl Accident from Afar	Carolyn Krause
	The Chernobyl Accident: Causes and Consequences	Anthony Malinauskas et al.
	Chernobyl from a Vienna Perspective: The Soviet View of the Accident	Thomas S. Kress
	Dynamic Analysis of the Chernobyl	Lester C. Oakes
	Environmental Aspects of the Chernobyl Accident	F. Owen Hoffman
Number Two, 1987	State of the Laboratory—1986: ORNL Engages in Collaborative Research	Herman Postma
	Positive Feedback in Nature	Donald Deangelis et. al.
Number Three, 1987	High-Temperature Superconductivity: ORNL Joins the Scientific Stampede	Carolyn Krause
	The Promise of Gas-Fired Heat Pumps for Buildings	Frederick Creswick
	Ground-Coupled Heat Pumps: ORNL Research Aims at Lowering Costs	Van Baxter et al.
	International Cooperation in Heat Pump R&D	Fred Creswick
	Technology Transfer and the Buildings Industry	Marilyn Brown

	Raising Roofing to a Science: ORNL's Roof Research Center	George Courville
	Foundations for Building Energy Efficiency	Jeff Christian
	ORNL's Earth-Sheltered Building Results Guide Foundation Research	Jeff Christian
	Improving Energy Efficiency in Homes and Commercial Buildings	William Mixon et al.
	The Performance and Economics of Superinsulated Houses	Carolyn Krause
	Radon Levels and Home Energy Conservation	Alan Hawthorne
	The Smart House Project	Carolyn Krause
	Magnetic Fusion Progress: A History and Review	John Sheffield
	Introducing Methanol-Fueled Vehicles	Ralph McGill
	Ultrasonic Diffraction Tomography for Imaging Tumors	Alan Witten
Number One, 1988	Toward a "Technological Commons"	Alex Zucker
	A New Licensing Approach	Jon Soderstrom
	Industrial R&D Consortia	Warren Siemens
	Local ORNL Spin-off Companies	Louise Dunlap
	Designing Chips by Computer	*Review* Staff
	Images of the Heart	F. F. Knapp
	"We Have the Best People Around"	J. Robert Merriman
	Microwave Processing of Ceramics	Carolyn Krause
Number Two, 1988	State of the Laboratory—1987: Gee Whiz Achievements	Herman Postma
	Susan Whatley: From Fast Track to Slow Boat	Luci Bell
	Imaging the World's Longest Dinosaur	Carolyn Krause
Number Three, 1988	Supercomputers in Scientific Research	H. Richard Hicks
	Using a Supercomputer for Theoretical Chemistry	Don Noid
	Supercomputing and Reactor Safety	Sherrell Greene
	Supercomputers in Materials Science Theory	Gayle Painter
	Fusion Calculations on Cray Supercomputers	Vickie Lynch
	Theoretical Atomic and Nuclear Physics	Christopher Bottcher
	Parallel Computers for Efficient Problem Solving	John Drake et al.
	Energy for Development: ORNL Returns to the Third World	Tom Wilbanks et al.
	Designer Steels for Advanced Energy Applications	Carolyn Krause
	New DNA Stain Aids Cell Studies	Luci Bell
Number Four, 1988	Waste Management and Remedial Action: A New Way of Doing Business	Tom Row
	The DOE Model	Lance Mezga

	Improving Waste Management Operations	Tim Myrick et al.
	Waste Management Technology Center	Robert Jolley
	The Hazardous Waste Technology Program	Phil McGinnis
	PCB-Eating Microbes	Terry Donaldson
	Radioactive Waste Management R&D	Allen G. Croff
	Grouts Solve Disposal Problems	Earl McDaniel
	ORNL's New Environmental Projects	Sid du Mont
	Remedial Actions for ORNL's Environment	Lanny Bates et al.
	QA in Waste Management	Jim Dumont
	Loss of Coolant: ORNL's Role in a Key Reactor Safety Experiment	John Cleveland
Number One, 1989	State of the Laboratory 1978–88: Years of Change	Alexander Zucker
	Competitiveness Begins at Home	Alvin Trivelpiece
	Market Research Aids Technology Transfer	Warren Siemens and Ernest Cadotte
Numbers Two and Three, 1989	This special issue on the life sciences of ORNL covers research in genetics, radiation biology, protein engineering, ecological sciences, energy and natural resources, compliance and risk analysis, earth sciences, microscopic interactions, dosimetry, metabolism, risk assessment, and evaluation of pollutant exposure and disease.	
Number Four, 1989	A Resurgence of Nuclear Energy?	Alexander Zucker
	Reactors Are Central to ORNL's Missions	Alvin Trivelpiece
	The Research Reactor Dilemma	Howard Kerr et al.
	The HFIR: Lessons Learned	Pete Lotts
	ORNL's Research Reactors	Carolyn Krause
	New Insights on Reactor Vessel Embrittlement	L. Mansur and K. Farrell
	The Oak Ridge Research Reactor: A Requiem	Luci Bell
	Isotope Materials for Research	Scott Aaron
	Nuclear Healing	Luci Bell
	Neutron Scattering at Research Reactors	Ralph Moon
	The Advanced Neutron Source: An Update	Colin West
	Modular HTGRs	F. J. Homan
	PIUS-BWR: Concept for a Passively Safe Reactor	C. W. Forsberg
	Advanced Controls for Nuclear Facilities	Jim White
	Global Warming and Nuclear Power	John Jones, Bill Fulkerson
	Oil Crises and Military Fuel Supplies	Jerry Hadder et al.

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Number One, 1990	Eureka! A Look at Inventing	H. C. (Chet) Thornton, Jr.
	Iron Aluminides and the Inventor of the Year	Carolyn Krause
	Human Behavior in Emergencies	John Sorensen
	Environmental Protection in China	Milton Russell
	Toward a One-Angstrom Electron Microscope	Steve Pennycook
	ORNL's Impact on Radiation Protection Guidance	Keith Eckerman and Alan Hawthorne
Number Two, 1990	State of the Laboratory—1989	Alvin Trivelpiece
	Scientific Visualization: New Insights By Computer	Joyce Francies and Ross Toedte
	Improving Detection of Airport Explosives	Carolyn Krause
	Microwave Processing of Radioactive Waste	Terry White
Number Three, 1990	ORNL Can Help Synthesize New Materials	Bill Appleton
	Robotics for Nuclear Reactors and Hazardous Environments	Frank J. Sweeney
	Examining Substitutes for Ozone-Depleting Chemicals	Van Baxter and Phil Fairchild
	Mechanisms of Radon Transport	Richard B. Gammage
	ORNL's Future Missions	Alvin W. Trivelpiece
Number Four, 1990	ORNL and Antarctica	Carolyn Krause
	Reducing Friction To Save Energy	Peter Blau
	Differing Structures of Amorphous Solids	Brian Sales and Lynn Boatner
	The Verdict on Acid Rain	Milton Russell
	ORNL's Contributions to NAPAP	David Shriner
Number One, 1991	ORNL's High-Temperature Superconductivity Pilot Center	Tony Schaffhauser and Louise Dunlap
	Superconductivity Research Successes	David Christen
	The Superconducting Motor	Carolyn Krause
	Waste Site Remediation: Are We Doing It Right?	Curtis C. Travis
	"No Option Would Satisfy Everyone"	Robin White
	Enzymes for Extracting Energy from Trash	Jonathan Woodward
Number Two, 1991	State of the Laboratory—1990	Alvin Trivelpiece
	Farewell to Herman Postma	*Review* Staff
	Single Crystals for Welding Research	Stan David and Lynn Boatner
	Science Alliance: A Vital ORNL-UT Partnership	Chester R. Richmond, Lee Riedinger, and Tom Garritano
	Profiles of ORNL-UT Distinguished Scientists	

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ORNL's Chemical Separations Group is synthesizing new compounds for extracting metals from solution.
See the article on p. 2.