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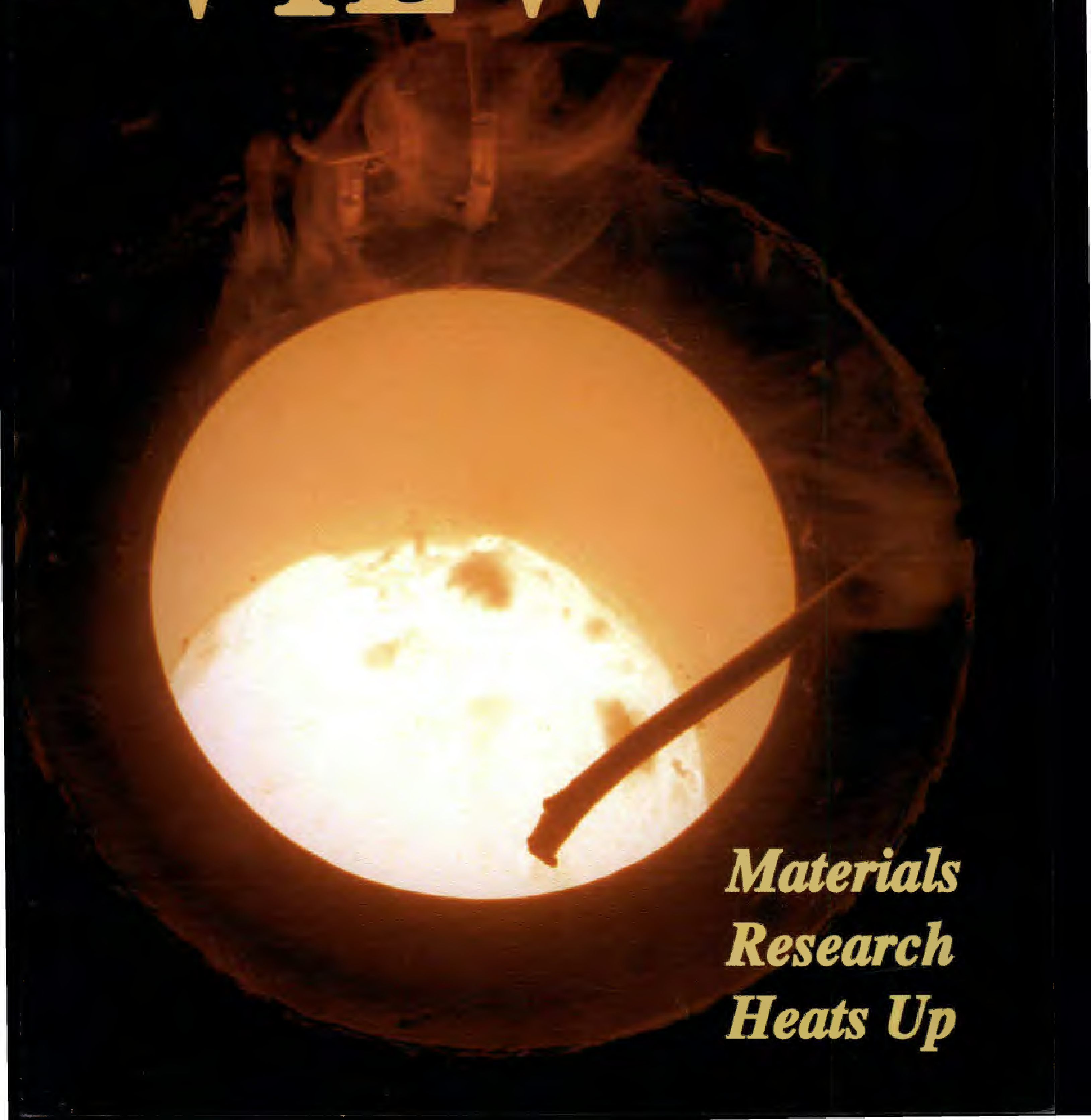

Materials Research Heats Up

COVER CAPTION

ORNL's materials research has produced some hot items lately, three of which were honored with R&D 100 awards in 1995. They are gelcasting for ceramic production, ceramic filters for advanced coal plants, and the Exo-Melt process, which is shown on the cover. Here, the process produces nickel aluminide by melting nickel, aluminum, and small amounts of alloying elements in a particular sequence. These and other materials research highlights are featured in this issue, starting with the article on the Exo-Melt process on p. 2. *Cover photo enhanced by artist Mark Robbins.*

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Editor
Carolyn Krause

Associate Editor
Bill Cabage

Consulting Editor
Bill Appleton

Designer
Linda Dickert

Technical Editing
Mike Aaron and Dale Norton

Electronic Publishing
Larry Davis and Gloria Glandon

Produced by the Information Management Services Organization

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FEATURES

DEPARTMENTS

Oak Ridge National Laboratory is a multiprogram, multipurpose laboratory that conducts research in energy production and end-use technologies; biological and environmental science and technology; advanced materials synthesis, processing, and characterization; and the physical sciences including neutron-based science and technology.

The Beauty in Technology Transfer

By William R. Martin
Vice President for Technology Transfer,
Lockheed Martin Energy Research Corporation

ORNL is working with the Semiconductor Manufacturing Technology (SEMATECH) consortium to improve the industrial process of making semiconductors for computers and other uses. Here, ORNL's John Caughman experiments with the deposition of polysilicon for possible use in making thin-film transistors.

Until about 15 years ago in the world of the U.S. government, technology transfer was a bad word, not a buzzword. It was deemed "inconsistent with mission of the Atomic Energy Commission" because it was perceived to detract from government research and draw talented personnel from national laboratories. But times have changed. Since the passage of federal laws in the 1980s, technology transfer has evolved into an important mission of national research facilities.

Oak Ridge National Laboratory, once an Atomic Energy Commission research facility and now a Department of Energy (DOE) laboratory, has always been ahead of the game in this arena. Since the 1960s, ORNL researchers have formed spin-off companies that manufacture and market technical products. As early as 1962, ORNL Director Alvin Weinberg established an Office of Industrial Cooperation to speed the adoption of scientific advances by the private sector. In the 1970s and 1980s, the federal government made it easier to transfer national laboratory technologies to the private sector by setting up mechanisms such as licenses, collaborative research agreements, and cooperative research and development agreements (CRADAs). Today the Oak Ridge Complex is a leader in technology transfer, responsible for nearly 20% of the total number of CRADAs entered into by DOE facilities. Oak Ridge also consistently places among the DOE leaders for its number of active licenses of patents.

Technology transfer is more of an art than a science. The beauty in this art lies in the ability of technology transfer to

Technology transfer turns the cutting of science and technology into the competitive edge of U.S. business.

Bill Martin considers technology transfer a sound business practice.

leverage the talents and funds of the government and private sectors to accelerate, enhance, and cuts costs of DOE mission work. The results benefit American industry because cutting-edge technologies from the national laboratories are being used to give U.S. businesses a competitive edge.

In Oak Ridge, technology transfer is not a business theory that just sounds good on paper; it's a sound business practice. Technology transfer comes in many forms such as licenses of intellectual property, CRADAs, personnel exchange, user facility agreements, technical assistance, work for others, and information exchange. The Laboratory continually pursues beneficial partnering with other entities through combinations of these mechanisms and through other novel approaches.

For example, ORNL collaborated with 3M Corporation to invent a "candle filter" for DOE's Fossil Energy Program that makes possible the next generation of cleaner, more energy-efficient coal power plants. Successful scale-up of the ORNL invention was the major technical constraint; however, this hurdle was overcome through a strategic technology transfer partnership. ORNL issued a competitive procurement for a development subcontract to mature the technology. The subcontract was granted to 3M because it met the primary criteria—it was willing to share the cost and it was committed to commercializing the ORNL technology.

According to Rod Judkins, an ORNL principal investigator, 3M provided six of the ten researchers assigned to the project and contributed expertise in materials science and filter technology. The DOE power plant program was thus advanced by an estimated 10 years, and ORNL work in developing heat exchangers for these power plants was accelerated by 5 years. (For more details on this technology transfer story, see "Technology Transfer" on p. 127)

Other examples of the transfer of ORNL technologies described in this issue are gelcasting (described in the article on p. 24) and production and use of nickel and iron aluminides (described in the article on p. 4). Like the candle filters, these technologies received R&D 100 awards in 1995. Gelcasting may become the process of choice for making ceramic products such as certain automotive parts, accelerator magnets, and possibly even artificial bone. ORNL-developed nickel aluminides are being used as furnace furniture for the manufacture of auto parts and as rollers for shuttling steel plates into furnaces for heat treatment.

Technology transfer projects are much more successful than some critics will admit. They are a cost-effective means of leveraging private and government dollars and talent to accomplish government missions efficiently while strengthening the competitiveness of private U.S. industry. Independent estimates place the market value of the ORNL-3M candle filters at $200 million per year by 1998 with a total market of approximately $7 billion from now to 2003. Because the ORNL-developed candle filter is the first of its kind to enter the market and is superior to competitors, it likely will dominate both the U.S. and world markets. DOE will benefit from considerable royalty income, 25% of which is eligible to be returned to the division that produces the licensable technology for maturation of other technologies. The top ORNL divisions receiving technology maturation funds from this source include Metals and Ceramics, Engineering Technology, and Health and Safety Research.

Product sales of inventions and services based on DOE–Oak Ridge technologies topped the $110 million mark in fiscal year 1995. The number of licenses that will produce such royalties is climbing steadily also, with more than a 50% jump from 1994 to 1995 alone.

Together, Lockheed Martin Energy Systems (which manages the Oak Ridge Y-12 Plant and K-25 Site) and Lockheed Martin Energy Research Corporation (which manages ORNL) have 287 CRADAs and 154 licenses. ORNL alone has 168 CRADAs and 130 licenses.

Department of Energy benefits from technology transfer continue to increase in number. Since 1992, the number of full-time equivalent employees who were actually guest workers contributing to mission work increased more than 80%. Partner contributions to CRADAs as a percentage of total R&D budget have also continued to rise since 1992.

Whatever the name—technology transfer, industrial partnerships, or research collaborations—partnering with the private sector, academia, and other government entities will remain a vital function for practicing the most efficient R&D possible and for turning the cutting edge of science and technology into the competitive edge of U.S. business. **ornl**

ORNL researchers Joseph Vought (left) and Vinod Sikka and Philip Morris' Seetharama Deevi, who was on a 1-year sabbatical at ORNL, developed the award-winning Exo-Melt process. This system enables low-cost manufacturing of advanced materials such as nickel and iron aluminides. *Photograph by Bill Norris.*

NICKEL ALUMINIDES:
BREAKING INTO THE MARKETPLACE

By Carolyn Krause

Nurtured by ORNL researchers for almost 15 years, nickel aluminides may have found their niche. ORNL's modified nickel aluminides are receiving considerable attention by the heat-treating industry in the United States and may have arrived just in the nick of time to make some companies more competitive. ■ Nickel aluminides are intermetallic materials that have long been considered potentially useful because, thanks to their ordered crystal structure, they are very strong and hard and melt only at very high temperatures. But they had a serious weakness: they were too brittle to be shaped into reliable components. Then, in 1982, ORNL researchers led by Chain T. Liu in the Metals and Ceramics Division found the secret recipe for producing a ductile nickel aluminide alloy: add

Joseph Vought inspects a coil cast from nickel aluminide at Harrison Alloys in Harrison, New Jersey.

Nickel aluminides are viewed as excellent candidate materials for furnace components used to manufacture parts by the automobile industry.

trace amounts of a few alloying elements in the right proportion. It was like turning peanut brittle into taffy. Their most important discovery was that the addition of a small amount of boron (200 parts per million) to a nickel aluminide alloy (Ni_3Al) makes the alloy highly ductile at room temperature.

ORNL's modified nickel aluminides have been attractive for industrial applications because they are lighter and five times stronger than stainless steel. They are also affordable: they contain no expensive, difficult-to-obtain materials of strategic value. Unlike standard alloys, which have a disordered structure that becomes even more random and weaker at increasing temperatures, nickel aluminides with their ordered structure become stronger as temperature rises to about 800°C. At high temperatures, they are resistant to wear, deformation, and fatigue, which is failure by cracking resulting from repeated stress or temperature.

Since the mid-1980s, ORNL's nickel aluminide alloy compositions have been licensed to about a dozen companies for various uses, ranging from processing glass to making dies for forming beverage containers and other shapes from metal. Automobile and tool companies have found ORNL's nickel aluminides especially appealing. The reason: because of its high aluminum content, this class of materials is virtually unaffected by gases containing oxygen or carbon at high temperatures. Because of their resistance to oxidation and carburization at temperatures up to 1100°C (2000°F), nickel aluminides are considered potentially useful materials for "furnace furniture"—assemblies used to contain parts during treatment at high temperatures to harden their surfaces. They are viewed as excellent candidate materials for tools for the metal-forming industry and for trays, belts, radiant tubes, mufflers, and other furnace components used to manufacture parts by the automobile industry.

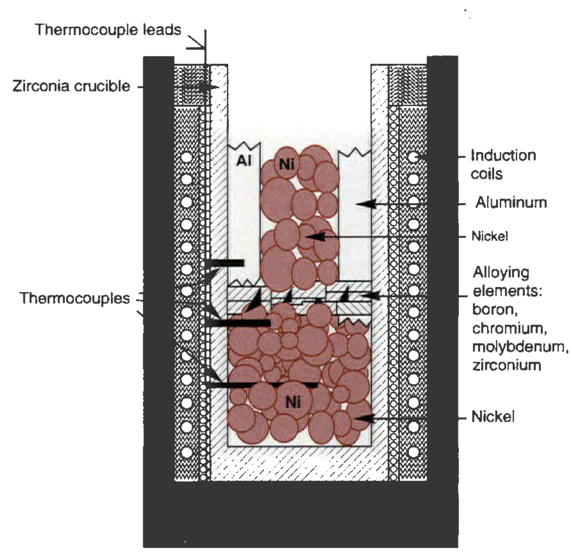
For nickel aluminides to find their niche, however, they needed yet another ORNL nudge. Researchers led by Vinod Sikka of the M&C Division were aware of the reluctance of metal producers to prepare nickel aluminides and felt compelled to overcome it.

"These vendors had experience adding less than 1% aluminum to steel to remove trapped oxygen," Sikka says, "but they resisted melting material that had as much as 8 to 12% aluminum. They feared that the molten aluminum would leak through tiny cracks in the furnace wall and attack the heating coils, possibly causing an explosion."

To address the safety concerns of the alloy preparation industry, Sikka and Joseph Vought developed a new process in collaboration with Seetharama Deevi, who was on a 1-year sabbatical at ORNL from the Research Center at Philip Morris in Richmond, Virginia. The development, called the Exo-Melt process, received a 1995 R&D Award from *R&D* magazine.

Exo-Melt Process

"Our process is a special way of loading the furnace crucible to take advantage of the heat that is generated in the reaction between nickel and



Schematic of the furnace-loading sequence employed for the Exo-Melt process to form modified nickel aluminide (Ni_3Al) by melting nickel, aluminum, and small amounts of alloying elements. A similar arrangement can be used to form iron aluminides.

aluminum, as in the case of reaction synthesis of materials," Sikka says (see sidebar on p. 12). "The reaction that produces NiAl liberates a large amount of heat and is, therefore, called an exothermic reaction. The heat of the reaction can be used to dissolve the alloying elements, such as boron, chromium, molybdenum, and zirconium. These dopants give the aluminide special properties like ductility and strength.

"What we want to produce is Ni_3Al, so we start by putting nickel on the furnace floor to provide the extra two atoms of nickel for each molecule of NiAl. For the next layer, we add the alloying elements. Then we add nickel, which is sandwiched between two stacks of aluminum at the top."

As the furnace elements are heated by induction coils, the exact temperature reached by each element depends on its properties. Nickel, which has a melting point of 1440°C, heats up to about 800°C as aluminum reaches its melting point of 660°C. As the aluminum melts and comes in contact with the heated nickel, NiAl forms, releasing large amounts of heat. In fact, droplets of NiAl, which has a melting point of 1639°C, begin to form and drip down along with unreacted molten aluminum. The superheated NiAl liquid dissolves the alloying elements on its way down. The molten aluminum also continues to react with the heated nickel and forms additional NiAl, which reacts with the nickel at the bottom of the furnace to form Ni_3Al.

"The key to the success of the Exo-Melt process is the furnace-loading sequence," Sikka says. "It makes possible the NiAl reaction that provides much of the energy for melting the rest of the elements in the furnace. The efficient use of heat from the NiAl reaction gives the Exo-Melt process several advantages. It saves energy, using only one-half to two-thirds of the power required by the conventional process. Because it melts the elements rapidly, it minimizes oxidation of the alloying elements and increases furnace life by minimizing time at high temperature. It allows ease of vacuum melting because all alloying elements can be loaded at the start. Best of all, it eliminates vendors' safety concerns in melting nickel aluminides."

General Motors–Saginaw Division uses modified nickel aluminide furnace trays to hold automobile parts transferred to a furnace for heat treating.

Scoring High on Industrial Tests

The Exo-Melt process has been communicated by ORNL to alloy preparation vendors, and journal articles have been published on the process (e.g., "Exo-Melt: A Commercially Viable Process," *Advanced Materials & Processes*, by Sikka et al., Vol. 147, No. 6, June 1995). The vendors using the Exo-Melt process to melt large heats of nickel aluminides and cast components are Alloy Engineering and Casting Company in Champaign, Illinois; United Defense in Anniston, Alabama; The BiMac Corporation in Dayton, Ohio; and Sandusky International in Sandusky, Ohio. The heats range from 150 to 3000 pounds.

Nickel aluminide parts made by the Exo-Melt process are already being used in the industrial world.

Nickel aluminide parts made by the Exo-Melt process are already being used in the industrial world on an experimental basis. At the General Motors–Saginaw Division facility in Saginaw, Michigan, automobile parts—valves, ball bearings, and gears—are heated in a carbon atmosphere in a furnace. "Carbon diffuses into metal," Sikka says, "and hardens the component surfaces to reduce wear."

Recently, an experiment was tried in a batch furnace at the General Motors–Saginaw facility.

General Motors concluded that nickel aluminide has twice the life of the HU steel that they've been using in their furnace.

Gears were loaded onto two different trays that were moved into the furnace. One tray was made of the chromium-nickel alloyed steel (HU steel) conventionally used by GM. The other was made of nickel aluminide. Both trays and their gears were subjected to a carbon source for the same time and at the same temperature. Then the gears and tray were moved to a tank of oil for quenching—they were cooled rapidly from between 800 and 900°C to 25°C, or room temperature. The gears or other parts being heat-treated to harden their surfaces are subjected to the heat-treatment cycle only once, but the trays holding the parts must endure hundreds of cycles in the furnace. The repeated thermal cycles—heating and rapid cooling—and the hardening effects of the carbon atmosphere caused the HU steel tray to fall apart in 6 months. The nickel aluminide tray was barely affected.

Sikka explains that, because of its high aluminum content, nickel aluminide forms a thin film of aluminum oxide on its surface. "This aluminum oxide film is like a brick wall," he says. "It keeps carbon from diffusing into the alloy because carbon has very low affinity for aluminum."

As a result of the batch furnace test, Sikka says, "General Motors concluded that nickel aluminide has twice the life of the HU steel that they've been using in their furnace trays. It is expected that continued tests will show that nickel aluminide lasts three to five times longer than the conventional material. Because use of nickel aluminide extends the life of furnace furniture, the furnace can be operated much longer before furniture replacements are needed, saving General Motors millions of dollars."

General Motors is considering the evaluation of complete nickel aluminide furnace assemblies consisting of a base tray, upper and lower grids, and support posts. The evaluation is part of a cooperative research and development agreement (CRADA), using funds from both DOE-ORNL and General Motors.

For another example, consider Rapid Technologies, a company in Newnan, Georgia, that manufactures

Rapid Technologies, a company in Newnan, Georgia, uses modified nickel aluminide to make rails for its walking-beam furnaces. Each heat-treating furnace has a mechanism for moving steel bars through the furnace by passing them from notch to notch along the rails from a room-temperature region to a very high-temperature region; in this way, the steel bars are softened so they can be formed into tools and horseshoes.

furnaces to be used for heating metal for manufacture of horseshoes, pliers, and wrenches. This company is using ORNL's nickel aluminide from United Defense to make rails for its walking-beam furnaces. The heat-treating furnace moves steel bars to a very high-temperature region, softening them so they can be formed into tools and horseshoes. The company has found that use of nickel aluminide rails in walking-beam furnaces has made possible the commercialization of its rapid-heating furnace technology. Because this technology provides rapid heating, less natural gas and process cooling water are needed, resulting in lower emissions and reduced energy use. Such technology should enable U.S. companies to be more competitive and to save jobs.

A major steel company is interested in using transfer rollers made of nickel aluminide in its steel-mill heat-treating furnace. There it heat treats steel plates at 800–900°C to soften them so they can be shaped into components for bridges and other structures. The current rollers, which are turned by a gear system to move each steel plate along through the mill, are fabricated from steel.

"These rollers eventually have two problems," Sikka says. "In the intense heat, they lose their strength, sag, and begin to wobble, jostling the steel plates. Also, they develop oxide particles on the surface that cause scratches. As a result, a large fraction of the steel plates produced at the steel mill are scratched. That's a problem because their competitors in Japan are selling steel plates that are not scratched."

The approach to the problem has been to shut down the furnace every third week for an inspection of the rollers. Sagging rollers are replaced with new ones. The needlelike oxides are ground out of the other rollers.

In the past year, the company has tried using rollers made from nickel aluminide in the mill. "Company engineers noticed that the oxides produced on the surface of the nickel aluminide are smooth," Sikka says. "Also, they concluded that nickel aluminides did not sag because they are three times stronger than the steel being used in the rollers.

"They hope to test a large number of nickel aluminide rollers soon. If the material performs as well as tests show, they should have to turn off the furnace only about once a year, not every 6 weeks, making it much more competitive in the steel industry."

Outlook

Nickel aluminides have come a long way since 1981 when Liu received $10,800 from ORNL's seed money program to find ways to make nickel aluminides ductile. Over $21 million has been spent on ORNL research that has successfully developed ductile nickel aluminides and an efficient process to produce them that is becoming acceptable to the alloy preparation industry.

"At the end of 1995, 50,000 pounds of Ni_3Al had been melted by industry," Sikka says. "Commercial sales of nickel aluminide are approaching a half million dollars. These amounts should climb rapidly now that a network of both nickel aluminide suppliers and users exists."

Commercial sales of nickel aluminide are approaching a half million dollars.

These successes would not have been possible without support from DOE's Office of Energy Efficiency and Renewable Energy, Advanced Industrial Materials Program; DOE's Office of Energy Research, Basic Energy Sciences Materials Program and the Energy Research Laboratory Technology Applications Program; and DOE's Office of Fossil Energy, Advanced Research and Technology Development Materials Program. These programs, especially Fossil Energy, also sponsored ORNL's research on iron aluminides described in the sidebar on p. 10.

Thanks to nudges from and networking by ORNL researchers, nickel aluminides appear to have found a niche. Clearly, they possess special properties that make them well suited for specific uses. Because they may help U.S. industry become more competitive and save jobs, ORNL's nickel aluminides are now breaking into the marketplace. **ornl**

ORNL's Iron Aluminides: An Emerging Success Story

Modified iron aluminides of industrial value were first developed at ORNL in the late 1980s. ORNL researchers were seeking a good substitute for stainless steel, which tends to corrode. They turned to iron aluminide alloys, which are resistant to air oxidation and corrosion. But they had to overcome this alloy's annoying tendency to break too easily at room temperature. They found that this brittleness is due to the formation of hydrogen and its diffusion into the alloy when aluminum reacts with moisture in the air. To decrease brittleness, they tried adding various alloying elements until they found the key ones that prevent or minimize the deleterious effects of reactions between aluminum and water vapor.

The resulting ductile iron aluminide earned an R&D 100 award in 1990 for Vinod Sikka, C. T. Liu, and Claudette McKamey. McKamey, who started at ORNL as a secretary and then became a metallurgist, made a key contribution: she discovered that small additions of chromium make iron aluminide more ductile. For her work, McKamey was named Inventor of the Year in 1989 by Martin Marietta Energy Systems, which then managed ORNL for the Department of Energy.

ORNL's iron aluminides (Fe_3Al) do not corrode readily in sulfur-containing environments because they form an aluminum oxide coating. "The aluminum oxide (Al_2O_3) film resists attack by sulfur," says Sikka, "but if the sulfur should break through, Al_2O_3 forms rapidly again to prevent the propagation of any sulfur attack. Our iron aluminide alloy provides higher resistance to sulfidation when exposed to hydrogen sulfide and sulfur dioxide gases than any other iron-based or nickel-based alloy."

For this reason, ORNL's iron aluminides are good candidates for filters in coal gasification plants. These plants produce a low-to-medium BTU fuel gas from coal. By-product ash must be removed from the gas by filters. As gas passes through the filter, sulfur compounds in the gas react with commercial metal filters, causing them to deteriorate. Because ORNL's iron aluminides resist attack by sulfur, they are being evaluated as coal gasification filters.

In 1990 Ametek obtained a license from Energy Systems to produce Fe_3Al powder to make filters. These filters, manufactured by the Pall Corporation in Cortland, New York, are being tested for coal gasification applications.

Other companies may find ORNL's iron aluminide desirable because of another selling point: it has a lower density and a higher strength-to-weight ratio than many stainless steels. These properties make iron aluminide an attractive candidate as a structrual material for some automotive components.

ORNL's iron aluminides possess three properties that also make them ideal as heating elements. They are highly resistant to oxidation and corrosion, and they have electrical resistivities that are higher than many commercially available heating-element materials. Evaluation by a private vendor showed that iron aluminide heating elements do not burn up as fast as commercial heating elements. In one experiment, an ORNL-modified iron aluminide element lasted almost three times as long as the commercial one.

Commercial use of iron aluminides as heating elements has been slow because of their limited ductility. But Sikka thinks ORNL research has found a solution to this problem.

"After iron aluminide wire is produced, one vendor found that the wire can be stretched only about 2 to 3% of its original length before breaking," Sikka says. "This problem limited its use in drawing it through a die to fabricate a heating element. But our laboratory research shows that, if the wire is run through hot water so that it's heated to about 100°C, its ductility improves ten times—from 2 to 20%."

Sikka says that, in a cooperative research and development agreement with Hoskins Manufacturing Company, he hopes it will be shown that heating elements can be made from iron aluminides by using both the Exo-Melt (see main story) and hot-water processes. If he's right, the iron aluminide saga might someday become as big a success story as that of nickel aluminide.

Claudette McKamey inserts an iron aluminide specimen into a furnace at ORNL. She is heating the specimen to determine the high-temperature strength and ductility of ORNL's modified iron aluminide alloy.

Aluminides: From Powders to Products Using Reaction Synthesis

Nickel and iron aluminides, which are lighter and stronger than stainless steel, are also valued because they resist heat. However, these alloys in the form of a sheet, tube, or block also resist being shaped into a final product. The reason: aluminides of nickel, iron, or titanium are extremely brittle at room temperature and, therefore, are nearly impossible to machine.

To solve this problem, Chain T. Liu of ORNL's Metals and Ceramics Division, who first developed ductile nickel aluminide alloys at ORNL, has spearheaded research in reaction synthesis using elemental metallic powders. Reaction synthesis is a chemical change in which an intermetallic alloy is formed from metallic powders using heat generated during the reaction. The method is considered attractive for producing aluminide products in desired shapes with little or no machining.

Reaction synthesis also can be used to produce aluminide products of high density for structural uses. Aluminides have many uses because of their low density and high strength at elevated temperatures. However, for structural applications requiring full density to bear heavier weights—for example, in cars, aircraft, and the space station—aluminides would not be of interest unless they were close to full density with minimum defects such as pores.

Working in collaboration with visiting scientists from Japan at different times, Liu has used reaction synthesis to produce a high-density, defect-free nickel-aluminide alloy. Traditional processes have produced nickel-aluminide alloys with a 97% density; such a porous material is too weak and brittle for many structural applications.

"By using reaction synthesis," Liu says, "we formed a ductile nickel-aluminide alloy product with a density as high as 99.9%."

Reaction synthesis for preparing alloys and forming them into products has other advantages. The self-generation of heat while making the alloy reduces the need for energy for material processing. Also, the cost of alloy and product preparation is lowered because of reduced energy requirements and the ability to form aluminide products directly from elemental powders.

In reaction synthesis of intermetallic alloys such as aluminides, fine powders of aluminum are mixed with the other metal of interest (iron, nickel, titanium) in the proper proportion for the desired compound (say, FeAl or Ni_3Al). After the powders are mixed in a rotating container called a ball-milling machine, the "green" unreacted samples are consolidated by pressing the powders together in a die, similar to forcing dough into a cookie cutter, to make a product of a desired shape. The resulting "green" disks are placed in a reaction chamber under vacuum and heated to 660°C, a temperature close to the melting point of aluminum powders.

At this point, reaction synthesis kicks in. Because the liberated heat raises the temperature of the neighboring layers of atoms of aluminum and the other metal to as high as 1400°C, the reaction is self-sustaining like that in a burning cigarette (except the alloy-forming reactions move faster—3 to 6 inches per second depending on the compound). Liu and his colleagues found that applying a few megapascals of pressure by a compression machine during reaction synthesis produces a material of near-theoretical density. "The idea," Liu says, "is to squeeze the pores out of the material so it's more like cheddar cheese than Swiss cheese."

More recently, Debra Joslin, Dewey Easton, Liu, and Stan David, all of ORNL's Metals and Ceramics Division, have been studying reaction synthesis of iron aluminides (FeAl and Fe_3Al). Using high-speed videotaping equipment, they studied the reaction behavior of iron aluminides during synthesis in air. They found that the reaction rate depends on compact composition and powder particle size; it increases with greater aluminum content, and it decreases with increasing powder size. They also found that pores formed in the reaction-synthesized products can be reduced by applying a compressive force.

Vinod Sikka and S. C. Deevi have shown that reaction synthesis, not under vacuum or pressure, can be used to produce ingots of nickel, iron, and titanium aluminides. Through forging, rolling, hot extrusion, and applied pressure, products can be cast from the ingots.

The Exo-Melt process described in the main article was developed by Sikka and Deevi by extending principles of reaction synthesis to the melting and casting of iron aluminide (Fe_3Al) and nickel aluminide (Ni_3Al). This process, which uses half as much energy as traditional processes and addresses safety concerns of the alloy preparation industry, was used at ORNL to melt and cast more than 100 ingots of Ni_3Al- and Fe_3Al-based alloys.

As a result of these successes, a unique facility has been developed at ORNL to study reaction synthesis of intermetallic alloys. The facility will be used to study processing parameters and the feasibility of forming near-net-shape products. Someday industry may find this emerging method of making products from powders too good to resist.

ORNL's Chrome-Moly Steel: A World-Class Material

ORNL's Vinod Sikka has won five R&D 100 awards. The first was for his work in 1974–75 at ORNL in developing a steel containing chromium, molybdenum, and other elements. It was developed for the U.S. government's Clinch River Breeder Reactor Project, which was to have been built in Oak Ridge but was canceled in 1983.

The award-winning chrome-moly steel was first manufactured and sold in the United States in 1983. The material was originally tested in boiler tubes at the Tennessee Valley Authority's Kingston Steam Plant in nearby Kingston, Tennessee.

It is now manufactured and marketed internationally by companies in France, Germany, Japan, and the United States for a total of over $100 million in sales. Because it doesn't easily corrode or deform at normal operating conditions, the material is used in utility boilers to produce electricity and oil refinery furnaces to make unleaded gasoline. Like Sikka, the steel is a winner, at least in certain applications.

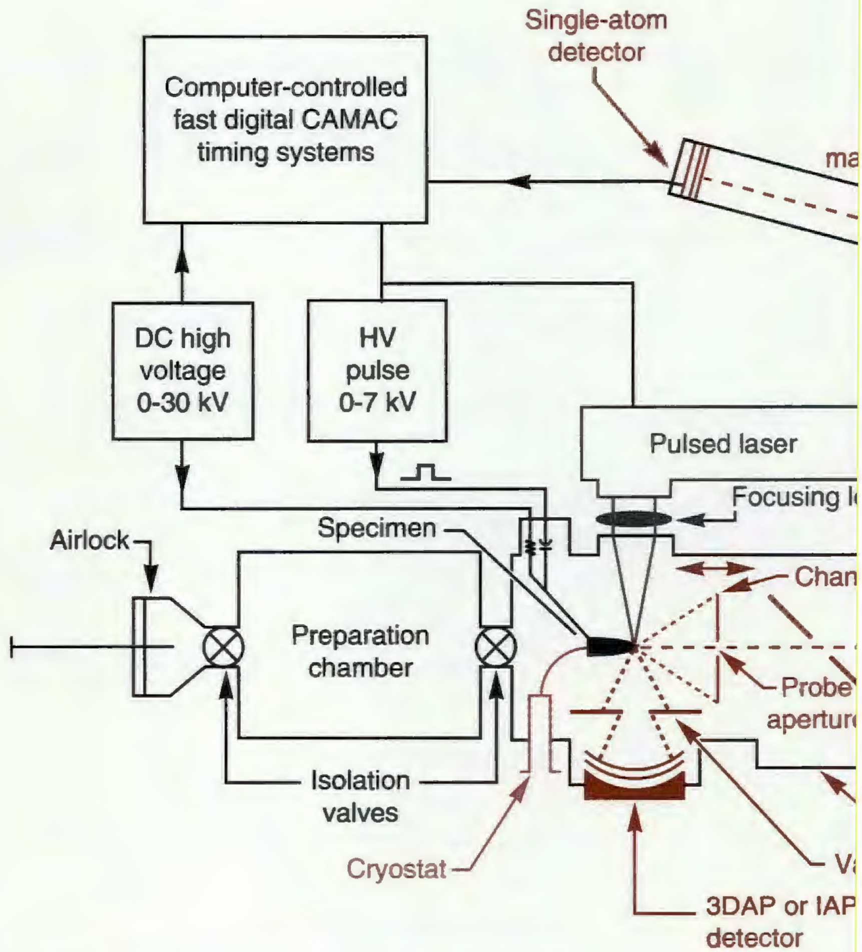
In this 1983 photograph, Vinod Sikka examines modified 9 Cr-1 Mo tubes after three years of operation at about 590°C in the Tennessee Valley Authority's Kingston Steam Plant. The 9 Cr-1 Mo tubes seen here are those with small transition pieces, easily identified by two adjacent weld seams. The tubes are still in place and performing well at the Kingston plant.

Seeing and Catching Atoms:

ORNL's Atom Probe Field Ion Microscope

By Michael K. Miller, Philippe J. Pareige, and Kaye F. Russell

The concept of the atom has existed since the 5th century B.C., but it was not until the 19th century that this concept was developed into a scientific theory. Even then, the ability to see individual atoms was considered an impossible task because they must be magnified a million times to be visible. However, in 1951 Erwin W. Müller, a professor at Pennsylvania State University, achieved this magnification after constructing a fundamentally new type of microscope that he called a field ion microscope. The device enabled him to see atoms on a routine basis. ■ In those pioneering days of the technique, the scientist was forced to sit in a completely dark room for 20 minutes to let his eyes become accustomed to the dark so that he could see the faint glow of the atoms on a phosphor screen. Fortunately, after the introduction of image intensifiers similar to those used in night vision binoculars, sitting in the dark was no longer necessary. In 1967, Müller and his colleagues further advanced the development of the field ion microscope by adding a mass spectrometer. The new instrument, called the atom probe field ion microscope (or atom probe, for short), made it possible not only to see but also to identify individual atoms. ■ The properties of materials can be



The ORNL atom probe includes a three-dimensional atom probe (3DAP) developed here.

dramatically changed by the presence of small quantities of certain elements, especially in the boundaries between a material's crystalline grains, called grain boundaries. Scientists have found that changes in properties can be related to changes in structure and composition at the microscopic level. Thus, metallurgists at ORNL and elsewhere were excited about the potential of this new instrument in characterizing the structure and composition of metals at the highest possible spatial resolution.

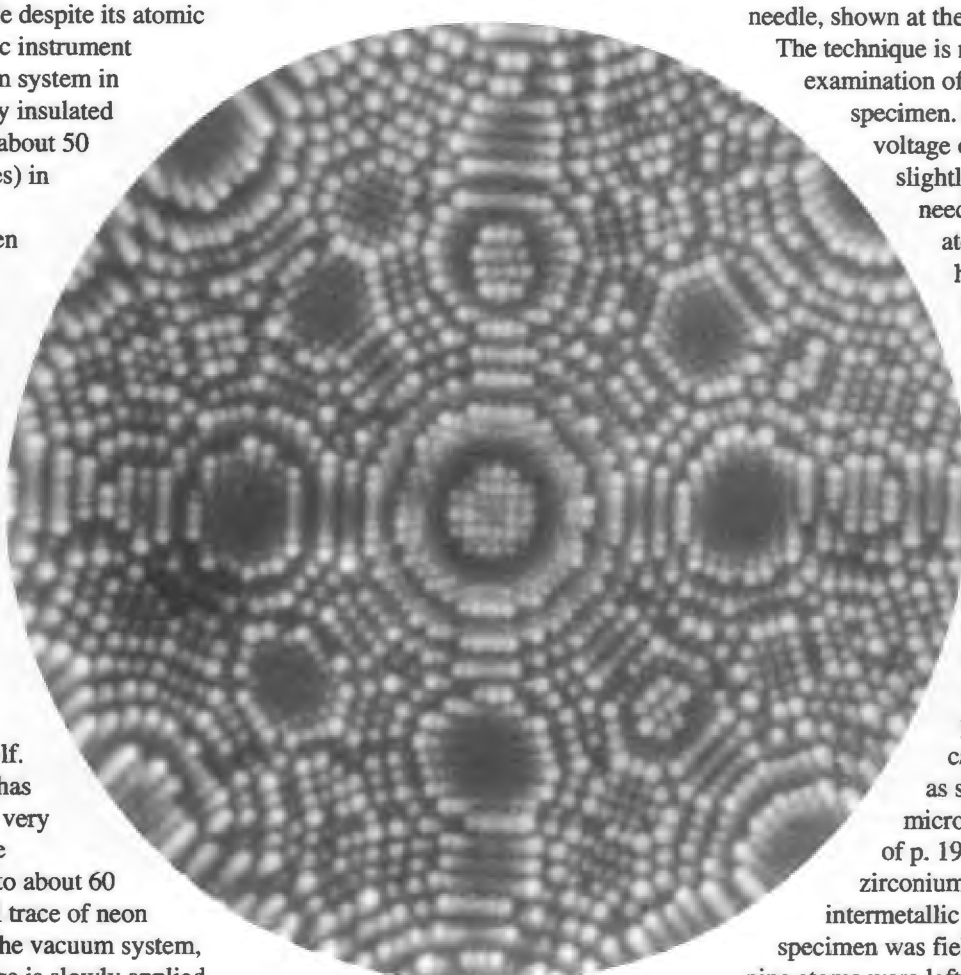
In 1981, Jim Bentley and Everett Bloom, materials scientists with the Microscopy and Microanalysis Scie Group in ORNL's Metals and Cera Division, recognized that the atom technique was developing into a po tool for characterizing metals and a They decided to add the capability their group to complement the othe powerful microanalytical technique their disposal. As a result of their initiative, the ORNL atom probe fa began operation almost 10 years ag

Today, this atom probe is used routinely to examine materials liter on an atom-by-atom basis. This fac has been used in a large number of

A Look under the Microscope's Hood

The design of the field ion microscope is remarkably simple despite its atomic resolution. The basic instrument consists of a vacuum system in which an electrically insulated specimen is placed about 50 millimeters (2 inches) in front of a phosphor screen. The specimen is in the form of a needle that is over 1000 times sharper than an ordinary household sewing needle. In fact, the end of the needle is so sharp that it cannot be seen by the naked eye or even a standard optical microscope; not surprisingly, fabricating these needles is an art itself.

Once the system has been evacuated to a very low pressure and the specimen is cooled to about 60 K (–213°C), a small trace of neon gas is let back into the vacuum system, and a positive voltage is slowly applied to the specimen. Because of the specimen's needle geometry, the neon atoms around the end of the needle are attracted to the positively charged specimen. If the voltage on the specimen is high enough, an electron may be removed from the neon atom, leaving a positively charged neon ion on the surface of the specimen. However, because the surface of the specimen also is positively charged, the neon ion is repelled rapidly from the specimen toward the phosphor screen. When the neon ion strikes the phosphor screen, it produces a spot of light. This process occurs continuously all over the specimen surface, and the resulting picture on the phosphor screen is called the field ion image. Consider a field ion image of a nickel-molybdenum (Ni_4Mo) intermetallic compound, shown above. Each of the individual dots in this image is an individual atom. One characteristic feature of the field ion image is the array of concentric rings. These rings arise from the intersection of the atomic planes in the crystal and hemispherical nature of the specimen surface, as seen in the computer simulation of the end of the needle, shown at the top of p. 19.



In this field ion micrograph of a nickel-molybdenum (Ni_4Mo) intermetallic compound, each dot is a single atom.

The technique is not restricted to examination of the surface of the specimen. By increasing the voltage on the specimen slightly higher than that needed to ionize the neon atoms or by applying high-voltage pulses of short duration, the surface atoms themselves can be ionized and removed, thereby revealing the interior of the specimen. This process, known as field evaporation, is the cornerstone of the atom probe technique. This process can be very carefully controlled, as shown in the micrograph at the bottom of p. 19. In this nickel-zirconium (Ni_7Zr_2) intermetallic catalyst, the specimen was field evaporated until nine atoms were left on the central atomic terrace. A series of short, high-voltage pulses were then applied to the specimen until one of the nine atoms (shown at the top left corner) was removed, leaving eight atoms on the terrace. This sequence of field evaporation was then repeated for the remaining atoms until only one atom was left on the atom terrace, as seen in the lower right frame. Field evaporation is also used to clean the specimen and remove any irregularities immediately after it is made.

The atom probe is particularly suitable for determining the location and distribution of elements within the structure of the alloy.

The only limitation on the type of material that can be examined with the field ion microscope is that it must be capable of conducting electricity to some extent. Thus, the technique may be applied to almost all metals and alloys, semiconductors, and a few special ceramic materials.

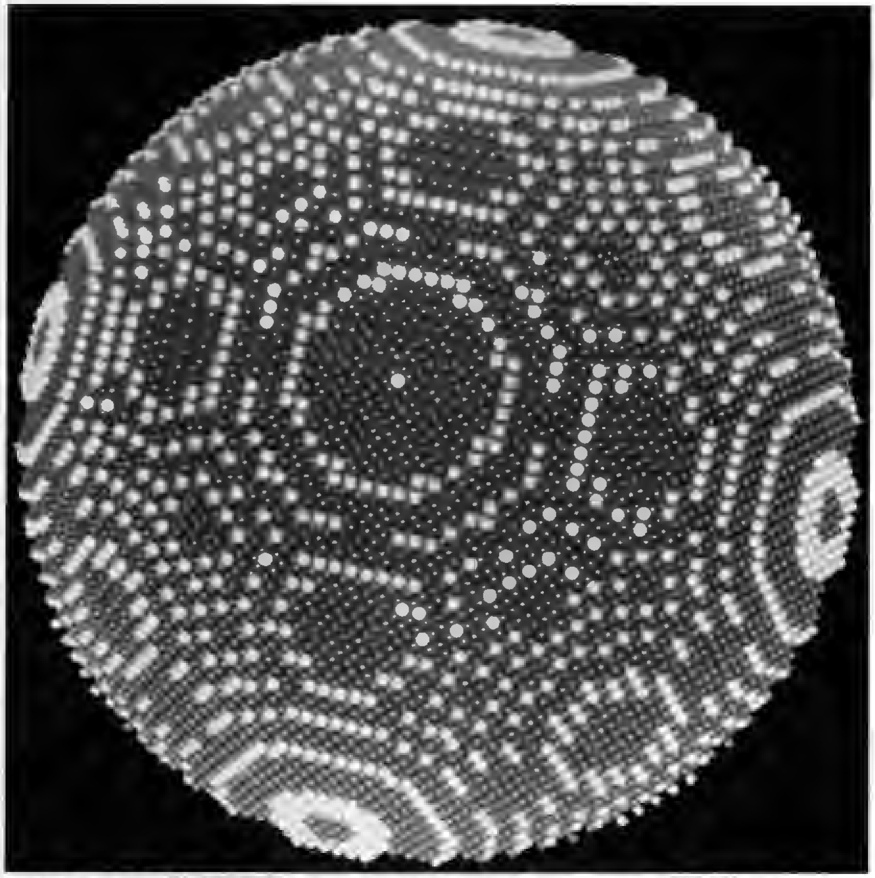
Although some information about the identity of the atoms can be deduced from the brightness of the atom in the image, a more precise method is to use the mass spectrometer section of the atom probe. By rotating the specimen, the image of the atom of interest is positioned over a small aperture in the phosphorus screen that acts as the entrance to the mass spectrometer. The atom can be removed by applying a 10-nanosecond, high-voltage pulse to the specimen to ionize all the atoms in a thin surface layer. Although all the atoms in this surface layer are removed and repelled toward the phosphor screen, only those atoms that pass through the small aperture and enter the mass spectrometer are analyzed. The effective size of this aperture can be selected to allow passage of just one atom or the atoms originating from an area a few atoms wide.

The identity of each atom is determined based on the time it takes the atom to travel from the specimen to the detector—a distance of a little more than 2 meters (7 feet). Because all the different types of atoms in the specimen have the same kinetic energy ($0.5\ mv^2$) when they leave the specimen, the elements of low mass (m) travel faster than the heavier elements and reach the detector first. However, this measurement requires sophisticated high-speed electronics because the typical velocity (v) of these atoms is approximately 300 miles per second. To perform this measurement with sufficient resolution to be able to identify all isotopes of each element in the periodic table, we use a clock that ticks 1 billion times a second and count the number of ticks. By repeating this process, the composition of small volumes may also be determined by simply counting the number of atoms of each element in that volume. A series of these small volumes can be collected to estimate the variation in composition in different regions of the specimen.

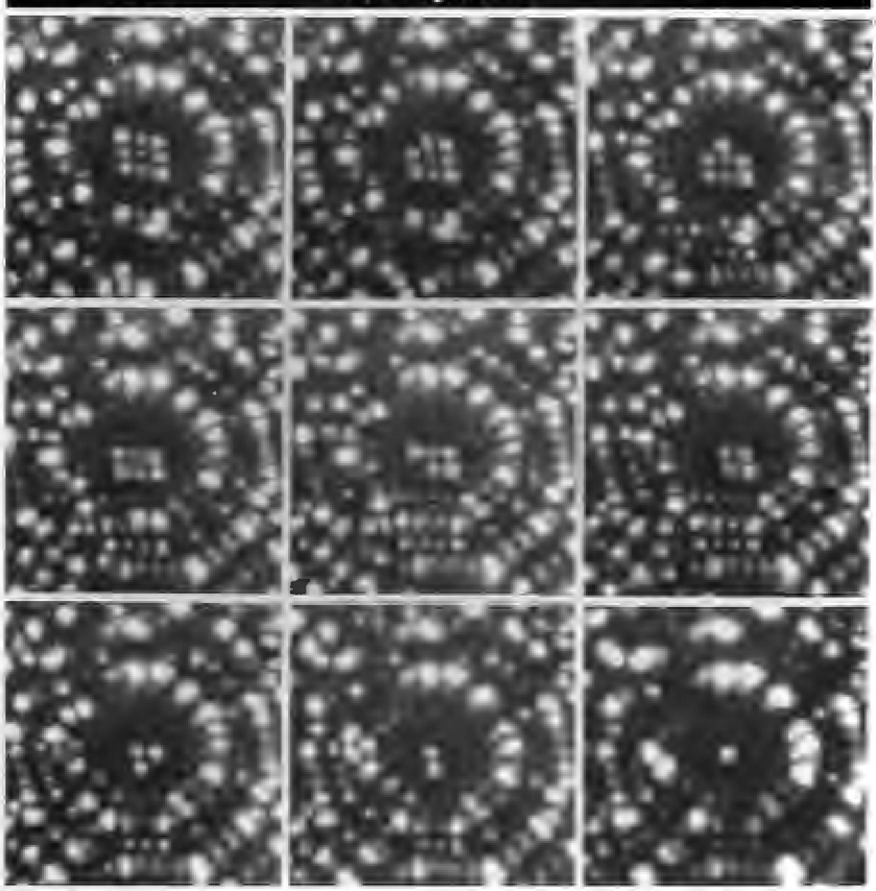
The Atom Probe's Applications

In today's rapidly changing world, there is a continuing need for new materials with improved properties. For example, materials that can be fabricated into various shapes and that can withstand high temperatures are needed in highly efficient engines being designed to reduce fuel use and emissions of pollutants. One of the standard approaches to achieving this goal is to design the alloy by adding different elements to refine a particular property. For example, in the commercial nickel-based superalloys used in turbine blades in modern jet engines, this refinement may include the addition of 10 or more elements to achieve the desired combination of properties, including strength, toughness, creep resistance, and oxidation resistance. The number of permutations of the possible interactions between this number of elements and other microstructural features makes it difficult to predict properties accurately. Therefore, it is desirable to determine the role of each of these additions experimentally. The atom probe is particularly suitable for determining the location and distribution of all these elements within the structure of the alloy.

A relatively simple example of this approach is the addition of boron to nickel aluminide (Ni_3Al). Pure Ni_3Al is extremely brittle at room temperature, limiting its technological application as a potential new lightweight high-temperature material. However, if as little as 200 parts per million of boron is added to the alloy, Ni_3Al becomes ductile, permitting it to be shaped into useful components without cracking (see related article starting on page 4 of this issue). This beneficial addition of boron may be understood by characterizing the distribution of boron throughout the alloy. The field ion micrograph on p. 20 reveals a region in a boron-doped Ni_3Al specimen that contains part of a grain boundary. The grain boundary is clearly seen in this micrograph because of the presence of a series of bright dots and the abrupt disruption of the concentric rings at the boundary where the orientation of the two crystalline grains changes. The identity of these bright dots may be uniquely determined by positioning the probe aperture over an individual bright spot in this image. Analysis of the atoms forming these dots in the mass spectrometer section of the atom probe revealed that they were individual boron atoms that had segregated to the grain boundary. This type of individual atom identification is possible only with this instrument. Atom probe analysis also revealed that boron was present at all the other disturbances in the crystal structure, including dislocations, low-angle boundaries, stacking faults, and antiphase boundaries. From these observations, we concluded that a fraction of the added boron atoms segregated to the grain boundary, where they acted as a type of

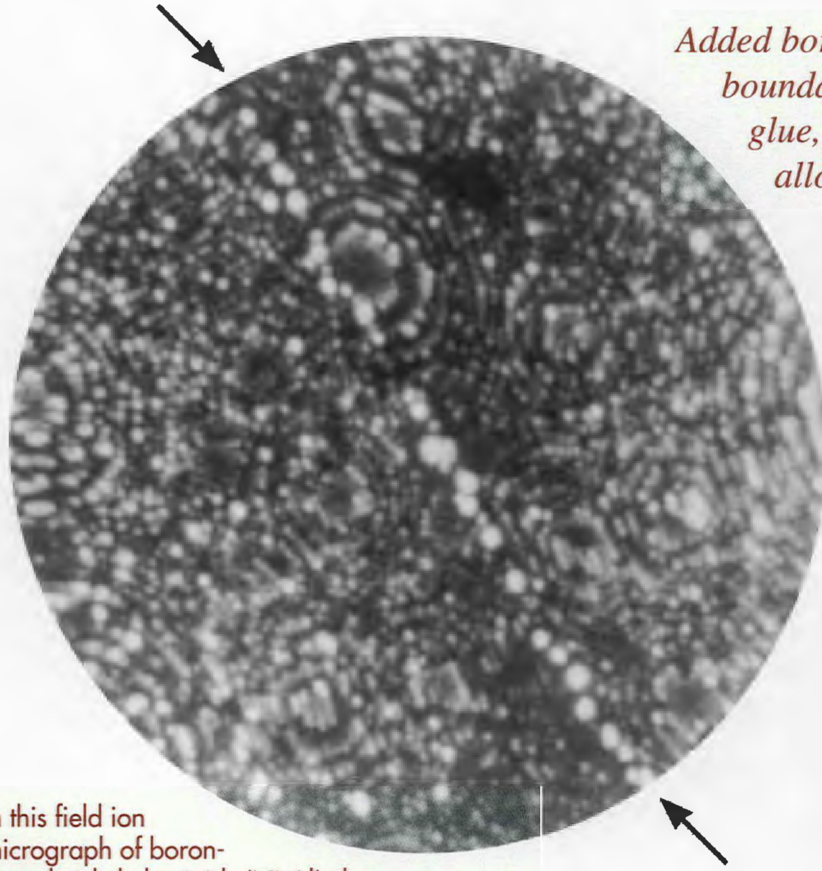


In this computer reconstruction of the sharp end of a needlelike field ion specimen, concentric rings appear because of the intersection of the atomic terraces with the surface of the specimen.



This field evaporation sequence shows the gradual removal of eight of the last nine atoms on the central atomic terrace of a nickel-zirconium (Ni_7Zr_2) intermetallic catalyst. One atom is evaporated from the central terrace between each pair of frames.

Added boron atoms segregated to the grain boundary, where they acted as a type of glue, preventing the nickel aluminide alloy from failing.



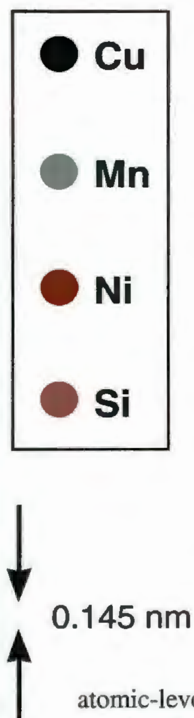
In this field ion micrograph of boron-doped nickel aluminide (Ni_3Al), the bright dots are individual boron atoms that have segregated to a grain boundary (arrowed).

glue at these otherwise weak points, thus preventing the nickel aluminide alloy from failing preferentially at these locations.

Unfortunately, not all elements are beneficial to the properties of a material. Some combinations can be potentially deleterious if the levels present are too high. For example, most steels used to fabricate the pressure vessel of a nuclear reactor contain small amounts of phosphorus and copper. Copper is not a typical impurity in commercial steels but can be present because of the use of copper-coated welding rods in the production of the welds in older reactors. Although these elements do not normally have a significant influence on the mechanical properties of the new pressure vessel, the distribution of these elements may change during the service lifetime of the vessel as a result of its exposure to a temperature of approximately 290°C for many years.

Two possible changes in the distribution of elements that could affect the long-term stability of the welds in these steels are the formation of extremely small copper-enriched precipitates and the segregation of phosphorus to the boundaries. The small copper precipitates strengthen the steel in much the same way as steel reinforcing rods strengthen concrete, but the precipitates also have the undesired side effect of making the steel brittle. Because embrittlement is not desirable in nuclear reactor vessels, it is important to determine whether these features are present, and if so, whether they change over the lifetime of the reactor. It is also economically important to know whether it is possible to extend the operating lifetime of a reactor pressure vessel without compromising safety. Because of the low service temperature, the size of early changes in the features approaches atomic dimensions. Therefore, the atom probe is an ideal technique for detecting and characterizing early changes in the microstructure of these materials.

Atom probe characterizations of a number of different pressure vessel steels reveal that they have extremely complex microstructures that involve a variety of small precipitates. Through use of the atom probe at U.S. Steel, Mike Miller and S. S. Brenner were the first to demonstrate that, in neutron-irradiated materials, the solubility of copper in the alloy was extremely low and the excess copper formed copper-enriched precipitates. Most recent research at ORNL demonstrated that these copper-enriched precipitates contained not only copper but also some iron, manganese, nickel, and silicon. This finding can be clearly seen in the computer reconstruction of the atom probe data of a volume of material that encompasses a precipitate, shown on p. 21. In this volume, the iron atoms (which are the majority of atoms in steel) have been omitted for clarity, and the extent of the entire volume analyzed is shown by the gray cylinder. The diameter of this



This type of atomic-level information has produced understanding of control parameters required to design alloys for special uses.

precipitate was determined to be only approximately 10 atoms across. Atom probe analysis has also revealed that the phosphorus had segregated to the grain boundaries but that its deleterious influence there was minimized because the grain boundaries were also coated with a thin film of molybdenum carbide and nitride precipitates, which prevents failure from occurring prematurely at these locations. This type of atomic-level information has produced a new level of understanding of control parameters required to design alloys that have properties needed for these types of applications.

More recently, Raman Jayaram and Miller have used atom probe field ion microscopy to demonstrate an important link between ultrafine-scale chemistry and a critical bulk mechanical property. If small amounts of molybdenum and zirconium are added to nickel aluminide in the proper proportions, the modified alloy is more ductile at room temperature, stronger and more resistant to deformation at high temperature, and less likely to react with oxygen. However, as the temperature reaches 777°C, the modified alloy is transformed from a ductile to a brittle material. This transition occurs at a lower temperature, 277°C, for undoped nickel aluminide. Using the atom probe, the ORNL researchers showed that the nickel aluminide matrix was severely depleted of zirconium and molybdenum. They found that the molybdenum precipitated out as spherical particles, and they obtained the first direct experimental evidence of zirconium segregation to dislocations in nickel aluminide when the material is annealed at elevated temperatures, 400 to 800°C. Identification of elements segregated to dislocations is nearly impossible to do by other techniques such as analytical electron microscopy. These changes in dopant positions and concentrations are responsible for property changes, such as loss of ductility.

This image is a computer reconstruction of an atom probe analysis of a small copper-enriched precipitate in a neutron-irradiated steel used in reactor pressure vessels. The precipitate contains not only copper (Cu) but also nickel (Ni), manganese (Mn), and silicon (Si) atoms. The iron atoms are not shown for clarity. The precipitate is approximately 10 atom diameters across.

Summary

These examples show it is possible to see and catch individual atoms routinely using the ORNL atom probe field ion microscope. Our technique enables complex materials to be characterized at the atomic level. Scientists from industry and universities have access to this state-of-the-art instrument through the Shared Research Equipment (SHaRE) program. This atom probe facility is the only one in the U.S. Department of Energy's national laboratory system that is available to outside users. Our ability to see and catch atoms is being shared with others.

Our atom probe facility is the only one in DOE's national laboratory system that is available to outside users.

Sponsors and Sources

The SHaRE program, including atom probe R&D, is supported by the DOE Office of Energy Research, Office of Basic Energy Sciences, Division of Materials Sciences.

Suggested reading

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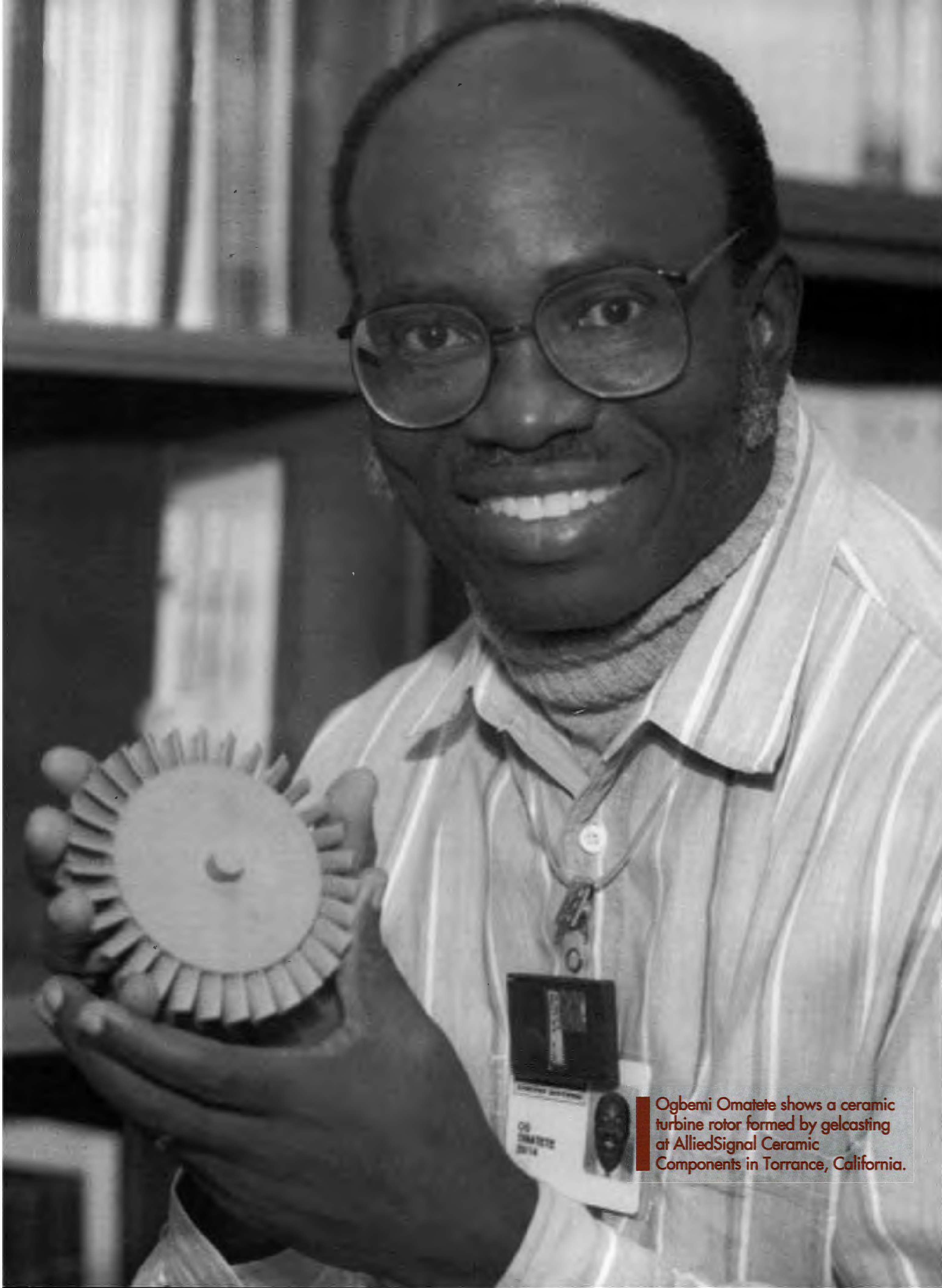
BIOGRAPHICAL Sketches

MICHAEL K. MILLER, a native of Beaconsfield, Bucks, England, is a senior research staff member in the Microscopy and Microanalytical Sciences Group in ORNL's Metals and Ceramics (M&C) Division. He has a bachelor of science and technology degree in materials science from the University of Bradford, England, and a D. Phil. degree in metallurgy from Wolfson College, University of Oxford, England. He was a Science and Engineering Research Council Fellow at Oxford's Department of Materials Science for two years. He came to the United States in 1979 to work at U.S. Steel Research Laboratories in Monroeville, Pennsylvania, and at the University of Pittsburgh. In 1983, he began atom probe research at ORNL. In 1986 he developed the innovative concept of the three-dimensional atom probe. His research interests include atom probe field ion microscopy, phase transformations, radiation damage, intermetallics, and nickel-base superalloys. He is president of the International Field Emission Symposium. Since 1985 (except for two years), he has been editor of the annual conference proceedings of the International Field Emission Society. He is the coauthor of two books: *Atom Probe Microanalysis: Principles and Applications to Materials Problems* (with G. D. W. Smith), published in 1989, and *Atom Probe Field Ion Microscopy* (with A. Cerezo, M. G. Hetherington, and G. D. W. Smith), published in 1996.

KAYE F. RUSSELL, a native of Clinton, Tennessee, is the principal technologist whose primary assignment is technical support and atom probe field ion microscopy research for the Microscopy and Microanalysis Group. She attended the University of Tennessee as a chemistry major. She came to ORNL in June 1967 as a Youth Opportunity Program student in the M&C Division's Welding and Brazing Laboratory. She transferred to the Metallography Group in the fall of 1967 and worked as a photographer's aide and then a metallographic technician. In 1982, she moved to the division's Radiation Effects and Microanalysis Group as a technician to prepare specimens for transmission electron microscopy. She began atom probe research in 1986. In 1993, she received a Martin Marietta Energy Systems Award for Technical Achievement.

PHILIPPE JEAN PAREIGE of Le Havre, France, is a postdoctoral researcher in the M&C Division's Microscopy and Microanalysis Group through the Oak Ridge Institute of Science and Education. He has a Ph.D. degree in physics from Rouen University in France. While working on his doctoral degree, he conducted research at the Laboratoire de Microscopie Ionique et Electronique (Ion and Electron Microscope Laboratory) of Rouen University. In 1991 he received the "young metallurgist" first prize from the Societe Francaise de Metallurgie et des Materiaux (French Society of Metallurgy and Materials Sciences) in Paris. His research interests include physical metallurgy, atom probe field ion microscopy, and nuclear pressure vessel steel surveillance.



Ogbemi Omatete shows a ceramic turbine rotor formed by gelcasting at AlliedSignal Ceramic Components in Torrance, California.

ORNL's Gelcasting: Molding the Future of Ceramic Forming?

By Carolyn Krause

The morning breeze brings music from the wind chimes outside your window. You wake up, and as you enter the bathroom, you are jolted when your bare feet touch the cold tile floor. Your feet are warmed in the bathtub during your shower. You become fully awake while sipping coffee from a mug. As you scoop cereal from a bowl, you daydream as you gaze at the brick hearth and the decorative figurines and flower vase on the mantel. ■ Welcome to the world of traditional ceramics, products made by baking mixtures of nonmetallic minerals. These conventional ceramics are made from natural raw materials such as clay. Ceramics were probably discovered when someone accidentally dropped into fire a clay pot or bowl shaped by hand and allowed to dry; the resulting object was observed to be hard and dense. Today some ceramics are still formed at a potter's wheel, which was invented 5000 years ago by the Sumerians, while others are made by slip-casting before being fired in a kiln. For centuries, ceramics have been used to hold food for cooking and eating, store beverages, and provide forms for artistic expression and decoration. ■ In the 20th century, a new kind of ceramics emerged. These ceramics are less visible, but they play an important role in today's technologies—the space shuttle, jet aircraft, power plants, and some cars and trucks. Americans call them "engineering ceramics" and the Japanese call them "fine ceramics." These advanced ceramics are formed by using high temperatures to process or densify inorganic, nonmetallic compounds, such as oxides, nitrides, borides, carbides, silicides, and sulfides. These materials are also known as "structural ceramics" because they are strong enough to bear weight.

Gelcasting is now receiving industrial and government support for early commerciali-zation.

"Engineering ceramics are not made from clay or other minerals," says Ray Johnson, leader of DOE's Ceramic Technology Project in ORNL's Metals and Ceramics (M&C) Division. "They are made from highly controlled, artificially produced raw materials. They are formed and densified by controlled processes such as hot isostatic pressing. They are used for products that have unusually demanding requirements, such as turbine blades and parts for rockets, nuclear reactors, and aircraft and automobile engines. Their microstructure is highly controlled. In short, they are appreciably different from traditional ceramics in their properties and in the way they are manufactured.

"I have a ceramic hammer in my office that I use to show that engineering ceramics are much stronger and tougher than traditional ceramics," Johnson continues. "I encourage visitors to drive nails into a piece of wood with my hammer, which is made from transformation-toughened zirconia. You wouldn't strike a nail with a porcelain vase."

In the Ceramic Technology Project, funded by DOE Energy Efficiency's Office of Transportation Technologies, Oak Ridge National Laboratory is developing technology for the cost-effective manufacture of reliable, lightweight ceramic parts for advanced engines. These engines will enable cars and trucks to use fuel more efficiently and reduce emissions. Our ceramic industry may someday be using advanced techniques to manufacture ceramic engine parts for cars and trucks and design even better ones for the future, thanks to ceramic-forming processes being developed in the M&C Division. The Laboratory's innovation in ceramic forming may be molding the future of ceramics manufacture.

Gelcasting—an advanced process for forming ceramics—was originally developed at ORNL to make complex-shaped automotive parts such as turbines. It is now receiving industrial and government support for early commercialization. The reason: this new process for making high-quality, complex-shaped ceramic parts shows promise for manufacturing ceramics at a lower cost than conventional forming techniques. In addition, gelcasting appears attractive for an increasing number of applications ranging from accelerator magnets to artificial bone.

"We developed gelcasting to produce small, complex-shaped turbomachinery for our sponsors," says Mark Janney of the M&C Division, who had the original idea for gelcasting. "Now, the applications are expanding to include simpler but larger shapes such as ring-shaped magnets for particle accelerators. Once we thought the largest shape we'd ever make would be the size of a loaf of bread. Now, we're being asked to make parts as large as a chair."

Consider the comments from Randall M. German, Brush Chair Professor in Materials at Pennsylvania State University. In a recent letter, German called gelcasting an "important advancement in ceramic-forming technology." He described gelcasting as "an innovative process for the production of ceramics" and as "an enabling technology that provides an avenue for implementing the use of ceramics in many advanced systems."

"Ten years from now," Janney says, "we believe gelcasting will be used as widely as slip casting, pressure casting, die pressing, extrusion, and injection molding are used today. Gelcasting will be part of the culture."

Not surprisingly, three industrial firms have obtained licenses to use ORNL's gelcasting technology, and the ORNL researchers are working with various companies in seven cooperative research and development agreements (CRADAs) and five informal collaborations. In addition, the technology has won prestigious awards.

In 1995, ORNL's gelcasting technology received an R&D 100 Award from *R&D* magazine, one of 79 R&D 100 Awards that ORNL has won since the competition began. The ORNL developers who were honored are Mark Janney, Ogbemi Omatete, Stephen Nunn, and Claudia Walls, all in the Ceramic Processing Group of the M&C Division. This was not their first award. In 1992, Janney and Omatete received an International Hall of Fame Award from the Inventors Clubs of America. Most recently, Omatete and Walls received a Federal Laboratory Consortium Award of Excellence for Technology Transfer.

Janney is a ceramic engineer with a Ph.D. degree from the University of Florida. Omatete is a chemical engineer and professor from Nigeria with degrees from Princeton University and the University of California at Berkeley. Nunn is a ceramic engineer with a Ph.D. degree from the University of Michigan; he has been involved with several CRADAs and is especially interested in machining gelcast ceramics before they are hardened.

Walls joined ORNL after earning an associate degree in mechanical engineering at a local community college. While working with researchers Robert Lauf and Terry Tiegs, both in the M&C Division, she became interested in ceramics. In 1988, Walls joined the team that was working on gelcasting. She has done much of the lab work that led to the rapid development of gelcasting. She received a Technology Transfer Award from Martin Marietta Energy Systems in 1989 for her early machining studies. She received a Technical Achievement

Award from Lockheed Martin Energy Systems in 1994 for her overall contributions to gelcasting.

Ceramics in the 20th Century

In the 20th century, it was discovered that ceramics produced in a controlled way from artificial raw materials—alumina, silicon nitride, zirconia—possess useful properties besides their resistance to heat. Some of these engineering ceramics achieve melting temperatures as high as 4000°F. They exhibit extreme mechanical hardness; for example, cubic boron nitride is almost as hard as diamond. They are resistant to corrosive chemicals. They are light. They are intrinsically strong. Unfortunately, like traditional ceramics, the use of engineering ceramics has been limited by their brittleness; but, thanks to recent developments in altering ceramic compositions, engineering ceramics are now much less brittle—like Ray Johnson's hammer.

In the late 20th century, new needs for ceramics have arisen. Shortages of fuel, energy price increases, and pollution have motivated the development of engines and power plants that use less fuel to operate. Gas turbine engines have been developed for power plants and aircraft and are being developed for automobiles because they use fuel more efficiently than spark-ignition engines.

ORNL's gelcasting is promising for lowering ceramic part manufacturing costs to a competitive level.

However, because these engines run at high temperatures and recover engine heat to minimize their use of fuel, they require parts that retain their strength at high temperatures. Only ceramics, not metals or even superalloys, can withstand the temperatures required for efficient automotive gas turbines.

Why are we not yet driving cars with high-temperature ceramic engines? Two problems have had to be solved. The first was that ceramics are normally brittle.

Mark Janney (left), Claudia Walls, Steve Nunn and Ogbemi Omatete received an R&D 100 Award for their gelcasting process, a new method for making high-quality, complex-shaped ceramic parts. *Photograph by Bill Norris.*

A gelcast part is soft enough to be machined quickly by less costly carbon steel tools.

Although they resist high temperatures, they can shatter when subjected to rapid and large changes in temperature—thermal shock—and other stresses. Can their chemical composition and structure be altered to allow them to hold up under such harsh conditions? Can reliable ceramic parts for cars be made?

The second problem is that the cost of manufacturing ceramic parts for the automobile industry has been much higher than the cost of making steel parts. Is there a low-cost method for manufacturing reliable ceramic parts that is competitive with mass production of steel parts for autos? Can we devise some way to make low-cost ceramic components?

Reliable ceramic parts can be made for cars, and ORNL has played an important role in the solution. Norton, AlliedSignal, and other ceramic companies have come up with new compositions and microstructures for silicon nitride that make the ceramic very reliable. Silicon nitride is the ceramic of choice for high-temperature engines because it is highly resistant to wear, deformation, oxidation, thermal shock, and decomposition at high temperatures. Matt Ferber and Ted Nolan, researchers with the M&C Division, have worked with Norton to test the reliability of its improved silicon nitride compositions at high temperatures and to determine the changes in microstructure that account for its improved properties.

ORNL's gelcasting is promising for lowering ceramic part manufacturing costs to a competitive level. The reason: it may allow industry to reduce the use of diamond tools to cut, shape, and finish ceramic products. Gelcast ceramics can be shaped by molding or machining before they are hardened by sintering in a hot furnace. Half the expense of ceramic manufacturing today comes from machining sintered ceramics by diamond tools. Machining itself must be done slowly to avoid damaging the ceramic. Although the expensive diamonds are harder than ceramics, they wear out quickly, requiring frequent replacement. And costs of labor and tools add up.

Illustrating a step in the gelcasting process, Omatete prepares to pour a ceramic slurry into a turbine rotor mold as Janney watches.

Gelcast ceramics can be formed in molds to get the precise shape desired because, unlike ceramics formed by other processes such as slip casting, gelcast ceramics shrink uniformly. Thus, the mold can be designed to compensate for shrinkage so that a ceramic part of the desired shape and size can be produced. "As a forming process," Omatete says, "gelcasting is limited only by the quality of the molds."

If machining is desired to improve on the final shape, gelcasting offers another advantage. After a gelcast part is molded and dried, it is strong enough not to crumble when manipulated yet soft enough to be machined quickly by less costly carbon steel tools. This process is called "green-machining" because it is applied to gelcast ceramics at the "green body" stage. After the gelcast parts are machined, they are hardened in a sintering furnace. The amount of final machining after firing is minimized, thus greatly reducing the need for machining with expensive diamond tools.

Green-machining of gelcast materials can be particularly useful for producing prototypes rapidly, providing custom manufacturing, and adding features to a cast part that would be too difficult or too costly to include in the mold.

Because the cost of machining ceramics could be significantly reduced using gelcasting, low-cost manufacture of ceramic components for engines may be feasible. Reducing manufacturing costs is critical to introducing ceramic manufacturing into the automobile industry. Efforts to determine the feasibility of commercializing gelcasting are now being pursued by the ceramic industry and the U.S. government.

Origin of Gelcasting

When Mark Janney was studying for his doctoral degree in ceramic engineering at the University of Florida, he learned about several ceramic processing techniques. Among them was injection molding, in which ceramic powder is mixed with wax or a polymer and forced into a mold. Polymers are used in ceramic processing because they bind ceramic powders together. Later in the process, the polymer (or binder) must be burned out. Because of the large amount of organic binder used in injection molding, the binder must be burned out very slowly to prevent cracking, significantly increasing the cycle time for producing ceramic parts by injection molding.

Janney was looking for a way to avoid steps in the injection-molding process (such as binder burnout) that lead to defects. He had experimented with methylcellulose, which is used in paints and ceramic glazes. When he mixed it with water, the mixture formed a gel when heated, just the opposite of Jello™, which forms a gel when cooled. "The gels were not very strong," Janney says, "but these experiments started me thinking about a solution-based process in which the initial material can be poured rather than forced into a mold."

Janney worked for a year and a half at Kennametals, Inc., in Greensburg, Pennsylvania, in the development of ceramics for cutting tools. Then he joined ORNL's M&C Division in 1983.

In 1984, Janney started research that eventually led to gelcasting. He knew the ceramics community at that time had a dire need for a forming method to replace injection molding for making large complex shapes such as turbine rotors. Many companies were trying to make silicon nitride and silicon carbide rotors by injection molding for DOE's Advanced Gas Turbine program. Rotors could be made by injection molding, but the yield of good product from this process was very low.

They came out of the furnace looking great. I knew then that the concept of gelcasting would work.

"It was not unusual," Janney says, "for a company to make 20 rotors in order to get one good one. Although this situation is common in a research environment, it was not encouraging to industrial people looking ahead to production.

In the mid-1970s, Janney had worked on injection molding of ceramics at the General Electric Company's Corporate Research and Development Center. Based on this experience and his observation at the University of Florida, Janney began thinking about alternative forming approaches. Says he: "I thought that a solution-based forming process could eliminate most of the problems associated with injection molding, especially the problems of binder removal and burnout."

Janney initially focused on developing gel chemistry because it is central to gelcasting. "My background in organic chemistry was limited," Janney says. "I did know that some polymers, such as poly (methyl methacrylate), could be made by polymerizing a monomer in an organic solvent. I conducted a series of trial-and-error experiments using several different monomers and solvents. I was able to make some gels, but they were not very strong."

A monomer is a relatively light and simple molecule that can combine with other molecules to form a polymer. A polymer is one of many natural and synthetic compounds that have a high

The first rotor we made came out of the furnace in great shape. Gelcasting had proven itself, at least in concept.

molecular weight because they consist of up to millions of repeated linked units, or monomers.

In 1985, Janney learned about a new group of monomers, called multifunctional acrylates. These are widely used in making printing inks (as on plastic cups and cereal boxes) and other coatings. He observed that gels made using the multifunctional acrylates were stronger than anything he had made so far.

"They were fantastic," Janney says. "The gels were hard and stiff, sort of like a hard rubber sole on your shoe. I mixed aluminum oxide (alumina) powder with the gel precursor solution, or premix, to make a ceramic slurry. I could get more than 50 volume percent alumina into the premix, an acceptable level of ceramic for the molding applications I was working on. When the slurry was gelled, it was very strong. You could drop a gelled part on the floor, and it would not deform or crack."

Janney dried the parts, burned out the binder, and then fired them at a high temperature. "They came out of the furnace looking great," he says. "I knew then that the concept of gelcasting would work. Next it was a matter of developing a water-based system."

In August 1987, Janney gained a collaborator in the gelcasting work. Ogbemi "Omats" Omatete, a professor of chemical engineering at the University of Lagos in Nigeria, came to ORNL on a 3-month sabbatical visit. During Omatete's visit, he and Janney worked to develop a water-based gelcasting system.

"Industrial ceramic manufacturers are used to working in water-based systems," says Janney, "so a water-based system would be accepted more readily as an industrial process." Says Omatete: "Water is easy to use, it's cheap, and it's environmentally friendly."

During his visit, Omatete tried to make water-based gels using more than 150 different compositions. Unfortunately, none of these made good gels. Finally, when they tried making gels based on the monomer acrylamide, they achieved instant success.

"We chose acrylamide because we knew it was used by biologists to make gels for electrophoresis for DNA fingerprinting," Omatete says. The acrylamide gels were quite strong and stiff. In addition, when Janney and Omatete tried to make ceramic slurries using the acrylamide gel premix, they discovered that the slurries were even more fluid than if they had made them in water alone. Recalls Janney: "Making a solids slurry that was 55 or 60 volume percent alumina was easy."

During the final 2 weeks of Omatete's sabbatical, the two engineers cast and fired an alumina rotor using the acrylamide-based gelcasting process. "The first rotor we made came out of the furnace in great shape," Janney says. "We knew we had a winning process. It was unheard of to make a good rotor the first time by injection molding. Gelcasting had proven itself, at least in concept."

Over the next 3 years, Janney, Omatete, and Albert Young, worked out the engineering details of the process and tried it on a variety of materials—alumina, quartz, silicon, silicon carbide, silicon nitride, sialon, zirconia, and ceramic composites.

"High solids loading is important," Omatete says, "because it minimizes shrinkage during firing of the part. The idea is to make the slurry as highly loaded with ceramic powder as possible and yet still be able to pour it into the mold," Omatete says. "We make it about the consistency of paint. Fortunately, gelcasting is a very forgiving process, and it will work over a range of solids loadings."

The key to the process is to add monomers, not polymers, to the initial solvent-ceramic powder mix. Here is the gelcasting "recipe," or flow chart.

Gelcasting Recipe

Mix and mill ingredients. Mix ceramic powder with water (or a nonaqueous solvent), a dispersant, and gel-forming organic monomers (later linked together to form a "binder," or polymer-water gel that binds the ceramic particles together).

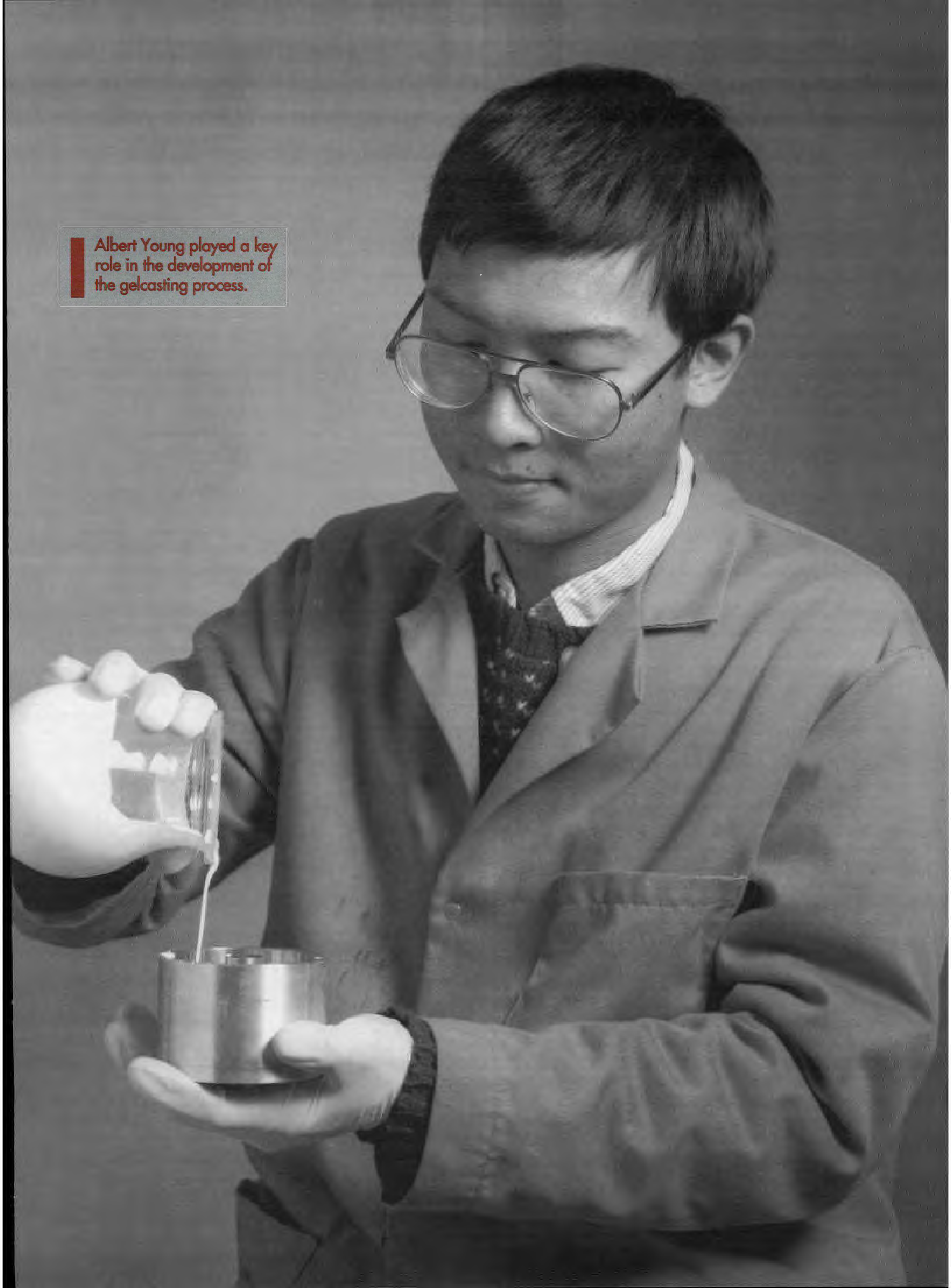
Deair. Place the mixture under a partial vacuum to remove air from it (otherwise bubbles could form, causing flaws in the final product).

Add catalyst. Add a "polymerization initiator" that kicks off the gel-forming chemical reaction.

Cast. Pour the ceramic slurry into molds made of metal, glass, plastic, or wax to cast it into desired shapes. "It's as simple as pouring muffin batter into a muffin pan," Omatete says.

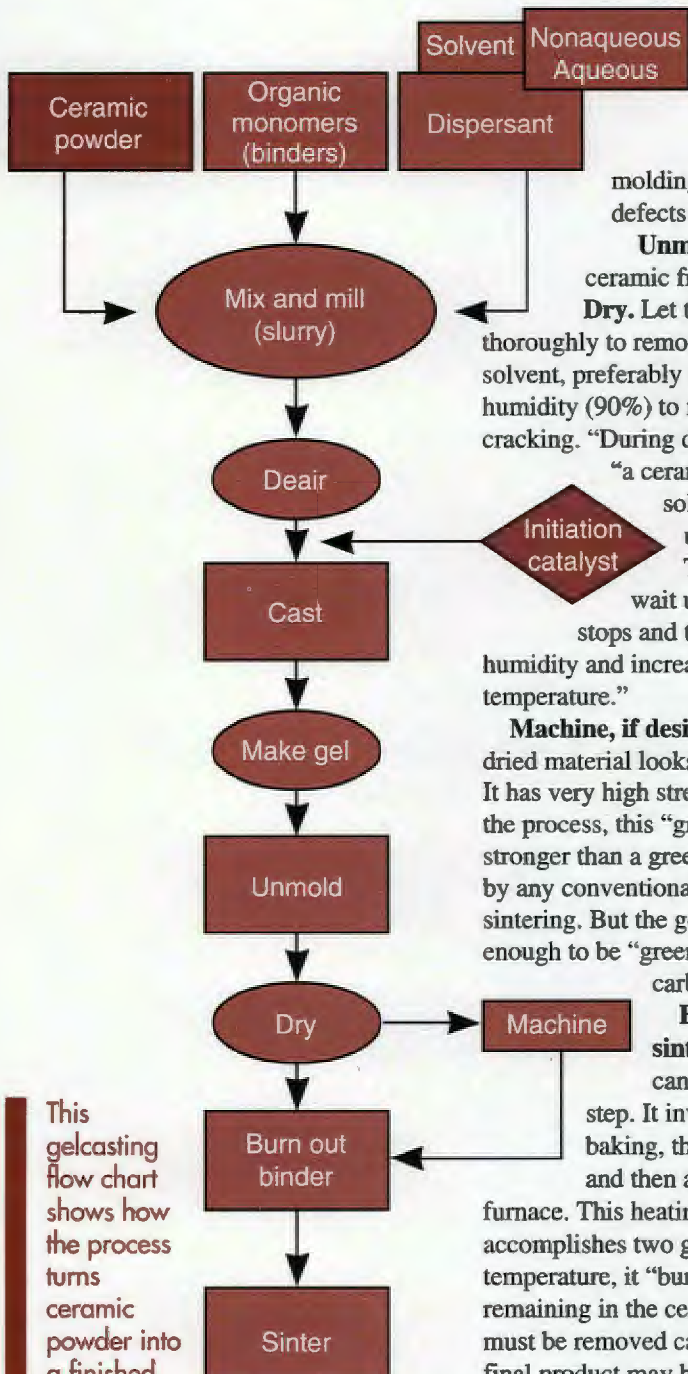
Create a gel. Heat the molds in a curing oven. The catalyst will cause the monomers to form large cross-linked polymer molecules that trap water, creating a rubbery polymer-water gel. The gel permanently immobilizes the ceramic particles in the desired shape defined by the molds. It is this setting step that gives gelcasting its name.

"By separating the mold-filling operation from the setting operation," Janney says, "gelcasting overcomes many of the problems associated with injection



Albert Young played a key role in the development of the gelcasting process.

Gelcasting Flow Chart



This gelcasting flow chart shows how the process turns ceramic powder into a finished product.

The products of gelcasting are defect free, uniformly dense, and very strong.

molding that can cause defects in the molded part."

Unmold. Remove the ceramic from the mold.

Dry. Let the cast ceramic dry thoroughly to remove most of the solvent, preferably at a high relative humidity (90%) to minimize warping and cracking. "During drying," Omatete says, "a ceramic slurry that is half solids should shrink uniformly about 3%. To speed up drying, wait until the shrinkage stops and then decrease the humidity and increase the air temperature."

Machine, if desired. The molded and dried material looks and feels like chalk. It has very high strength. At this stage of the process, this "green body ceramic" is stronger than a green body ceramic made by any conventional technique before sintering. But the gelcast ceramic is soft enough to be "green-machined" by carbide steel tools.

Burn out binder and sinter. The last two steps can be combined into one step. It involves firing, or baking, the ceramic at 550°C and then as high as 1800°C in a furnace. This heating process accomplishes two goals. At the lower temperature, it "burns out" the polymer remaining in the ceramic; this polymer must be removed carefully or else the final product may have defects and cracks. At the higher temperature, the furnace's intense heat sinters the ceramic, making it hard and dense.

"The slurry can be processed in an entirely closed system to keep the contaminants out," Janney says. "The equipment used in gelcasting is similar to that used in conventional ceramic processing.

"The advantages of gelcasting over conventional ceramic processing methods," he adds, "are that its products are consistently defect free, uniformly dense, and very strong and that the process is able to form very large parts."

On August 18, 1989, Martin Marietta Energy Systems (now Lockheed Martin Energy Systems) licensed ORNL's gelcasting technology to Coors Ceramics Company of Golden, Colorado. However, the ORNL ceramic engineers soon realized they had a problem with their water-based gelcasting recipe. Several ceramic companies had expressed concern about using the monomer acrylamide because it was known to be toxic to the human nervous system. To solve the problem, Omatete and Janney selected seven different monomers as possible substitutes for acrylamide.

Omatete found that methacrylamide is relatively safe because it is not easily absorbed through the skin, as is acrylamide. Says Omatete, "Methacrylamide is rated as safer than common chemicals like gasoline. We decided to use it as our monomer for future industrial applications."

Three patents have been issued for gelcasting. The first was to Janney for nonaqueous gelcasting; it was issued in 1990. Two others were issued to Janney and Omatete for aqueous gelcasting in 1991 and 1992.

Gelcasting Passes an Industrial Test

In 1990, AlliedSignal Ceramic Components entered into a cooperative research agreement with the ORNL ceramists. The company sent ceramic powders to ORNL for gelcasting, and the gelcast parts were returned to AlliedSignal for its evaluation. In mid-1991, AlliedSignal approached the ORNL ceramists about making a joint proposal to the National Institute of Standards and Technology's (NIST's) Advanced Technology Program (ATP). The partners submitted the proposal in September 1991, and AlliedSignal received an ATP grant in June 1992.

In December 1993, Omatete had a rare opportunity. As part of the ATP project, he was invited to spend 3 months at AlliedSignal Ceramic Components in Torrance, California. The purpose of the stay was to determine if gelcasting was a viable method for fabricating silicon nitride turbine rotors.

Silicon nitride was selected as the material for blades and vanes in these turbine rotors because it has the required strength and creep resistance at 1370°C. Its light weight and wear resistance are additional advantages. Such turbines are being manufactured for use in on-board engines in military and commercial aircraft. These engines provide auxiliary power when an aircraft sits idle on the tarmac and emergency power when a main engine fails.

AlliedSignal engineers were interested in investigating gelcasting and comparing it to two turbine-casting methods they had been using—injection molding and slip casting.

In injection molding, the ceramic powder is mixed with a polymer, forming a very thick fluid. This fluid cannot be poured into a mold, as is done with gelcasting. Instead, the fluid must be forced, or injected, into the mold under high pressure.

The AlliedSignal engineers noted that gelcasting did not have two problems that plague injection molding. One problem is the removal of the binder (the polymer that binds the ceramic particles together). In injection molding, the binder can be as high as 20% of the weight of the ceramic; in gelcasting, the binder takes up only 3 to 4%. In injection molding, burning out the binder may take a week, compared to less than a day for a gelcast ceramic. Binder burnout is tricky in injection molding, because if the temperature is too high, the part can sag, warp, and crack before the binder is completely removed. Defects and cracks can also develop in other stages of the injection-molding process such as drying. Such problems are rarely seen in gelcast ceramics if they are properly dried.

"Gelcasting forms a higher percentage of defect-free parts than injection molding because the slurry is poured, not forced by high pressure, into the mold," Omatete says. "In gelcasting, the mold-filling step is separated from the setting step. The slurry doesn't solidify until the molded material is placed in the curing oven. In injection molding, the mix must be superheated so it flows easily into the mold. But then heat must be removed so that the mix cools enough to solidify in the mold. The competition between the mold-filling and heat-removing processes can form defects in the material."

In slip casting, the starting powders are suspended in water to form a "slip." The slip is poured into a porous mold made of plaster of paris or another appropriate material. The capillary action of the porous mold draws water from the slip, which forms a solid layer inside the mold. When the part is as thick as desired, the rest of the slip is poured from the mold. The part is dried partially in the mold until it has shrunk away from the mold and is rigid enough to be removed and handled.

The AlliedSignal engineers noticed that slip cast turbine blades had density variations, but the gelcast blades were uniform.

"The AlliedSignal engineers," Omatete says, "noticed that slip-cast turbine blades had density variations, but the gelcast blades were uniform. They also were impressed that the gelcast material was stronger than the slip-cast material."

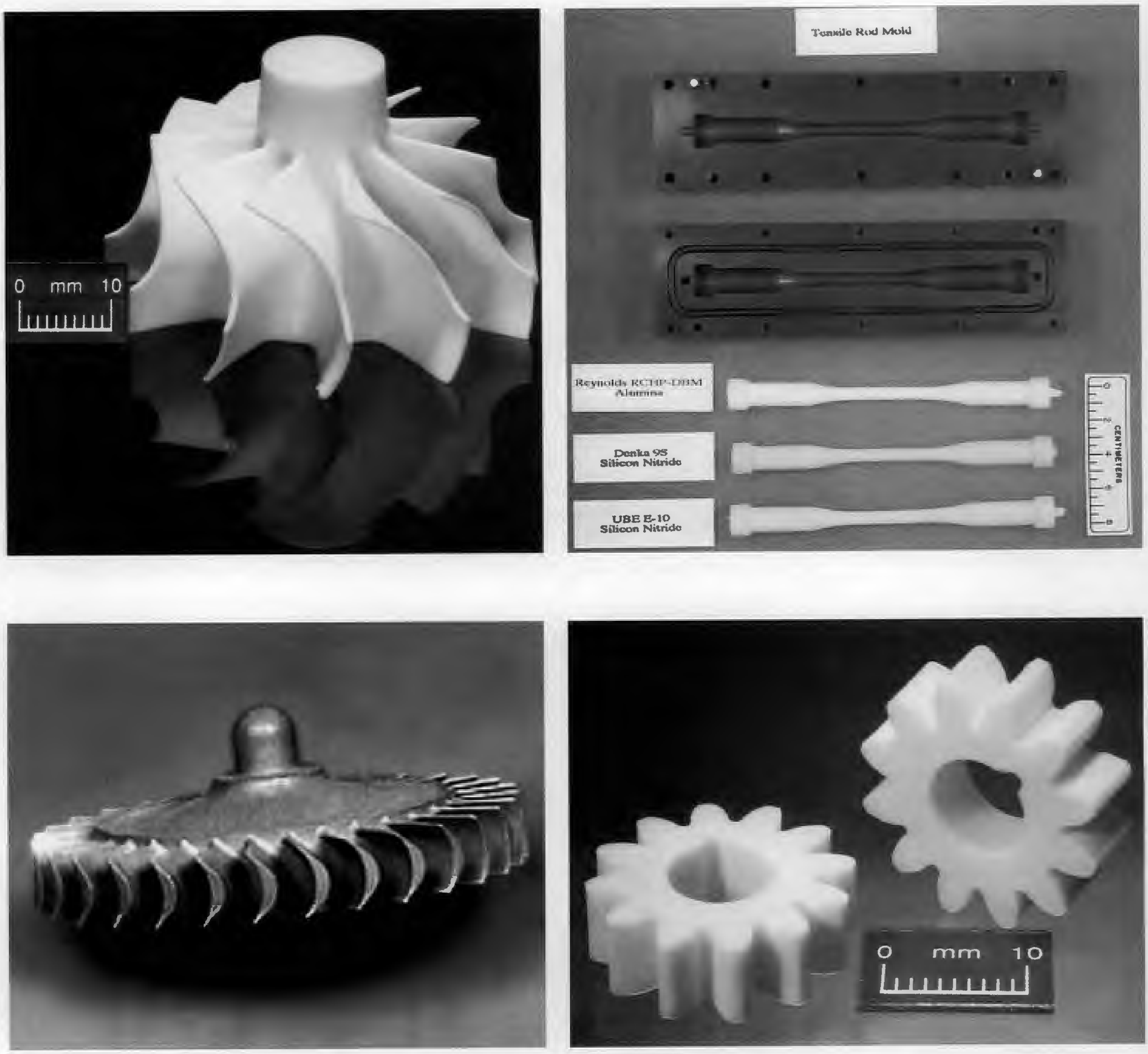
Omatete's 3-month stay involved a harrowing experience: the January 17, 1994, earthquake in southern California. "My bed shook for more than 30 seconds," Omatete says, "It was pretty scary."

The results of the gelcasting process proved anything but shaky. AlliedSignal engineers "were high on our process," Omatete says. And that was a high point for him.

Maxine Savitz, general manager of AlliedSignal Ceramic Components, wrote a letter praising Omatete's efforts to move an ORNL-invented technology into the marketplace. She states that Omatete's daily interaction was invaluable and accelerated the application of gelcasting as a potential manufacturing process at Ceramic Components.

Gelcasting Moves into the Marketplace

The ORNL ceramists have demonstrated that gelcasting can be used to form parts from a variety of materials,



Complex parts made by gelcasting include, from top left clockwise, an alumina turbocharger rotor, silicon nitride tensile test bars, alumina gears, and a silicon nitride turbine wheel.

including ceramics, superalloys, metals, and fiber-reinforced ceramic composites. They have produced gelcast ceramics that included silicon carbide, silicon, silicon nitride, aluminum titanate, and sodium zirconium phosphate. They have also made tin oxide and iron oxide (ferrite) forms.

AlliedSignal Ceramic Components now has a license to develop and use gelcasting for the manufacture of turbomachinery for aircraft. Funding for this development work comes from NIST's Advanced Technology Program and the Advanced Materials Program in the Department of Defense's Advanced Research Project Agency (ARPA). The goal of this project is to commercialize gelcasting.

LoTEC of Salt Lake City also has a license to use gelcasting to make special automotive parts from sodium zirconium phosphate.

One of the most exciting nonautomotive applications of gelcasting, Janney says, is the development of accelerator magnets made of ferrite—a ceramic based on iron oxide. "Ferrite is used for soft magnets like those used in the heads of tape recorders," Janney says. "They are also used in accelerators to shape charged particle beams for research in high-energy physics."

The ORNL researchers are working on the magnet project in a CRADA with Ceramic Magnetics, Inc., of Fairfield, New Jersey. The goal is to use gelcasting to fabricate circular magnets—more than 50 centimeters, or 20 inches, in diameter—from ferrite for a high-energy physics accelerator.

Slip casting and die pressing have been considered for magnet fabrication, but it was feared that, after the large, heavy magnet parts were cast, they would break easily when moved to the sintering furnace. However, the gelcast parts are strong enough to be moved and handled without problems.

"Gelcasting," says Janney, "enables people in the ceramics industry to do

■ ORNL ceramists have shown that gelcasting is well-suited for fabricating ring magnets for a particle accelerators.

Omatete discusses gelcasting and efforts to transfer the technology to industry. His audience includes, from right, Secretary of Energy Hazel O'Leary, ORNL Director Alvin Trivelpiece, and Frank Munger, science reporter for the *Knoxville News-Sentinel*. Secretary O'Leary helped to expedite Omatete's 3-month stay in Torrance, California, so that he could guide AlliedSignal Ceramic Components in using gelcasting to form ceramic turbine rotors.

things they wouldn't otherwise be able to do."

Other nonautomotive applications are being developed. Under a CRADA funded by DOE Energy Efficiency's Office of Industrial Technologies, Norton Inc. is collaborating with the ORNL group to produce complex-shaped silicon carbide parts for semiconductor wafer processing. Another application now being probed is the use of gelcasting to manufacture artificial bone to replace badly fractured human bones.

Omatete, Janney, Nunn, and Walls are extremely busy working on five gelcasting collaborations and four other gelcasting CRADAs with various industrial partners. Most of the work involves using gelcasting to develop powders or parts for automotive applications.

The ORNL researchers are serving as consultants to AlliedSignal Ceramic Components for the gelcasting commercialization project, which is receiving funding for 2 years from ARPA through the Office of Naval Research.

Project participants include a consortium consisting of AlliedSignal Ceramic Components, universities, private users and manufacturers of ceramic powders and engine parts, and ORNL. They are exploring large-scale production of silicon nitride turbomachinery parts for gas turbines by gelcasting. The automobile industry will more likely be interested in building cars and trucks with gas turbines if the cost of manufacturing ceramic parts can be lowered. Gelcasting may be the key to making ceramic parts manufacturing competitive with steel parts fabrication. The goal of the $7 million ARPA project is to determine the feasibility of scaling up and commercializing ceramic production by gelcasting.

The ORNL gelcasting group also is involved in two CRADAs with Advanced Ceramic Research, Inc. of Tucson to investigate rapid prototyping. "With gelcasting," Omatete says, "we can quickly fabricate new shapes for new designs of automobile parts so they can be studied and tested."

In one CRADA with this company, researchers will investigate how well the company's injection stereolithography process can do rapid prototyping using gelcast slurries. In the other CRADA, computer-aided design (CAD) tools will be used to green-machine gelcast parts.

"An object is designed on a computer using CAD," Omatete says, "and then the computer operates a computer numeric–controlled machine that cuts and shapes the gelcast ceramic. In this way, the ceramic is green-machined according to the computer design." You could call it high-tech pottery.

Things are shaping up well for ORNL's excellent cast of gelcasting researchers.

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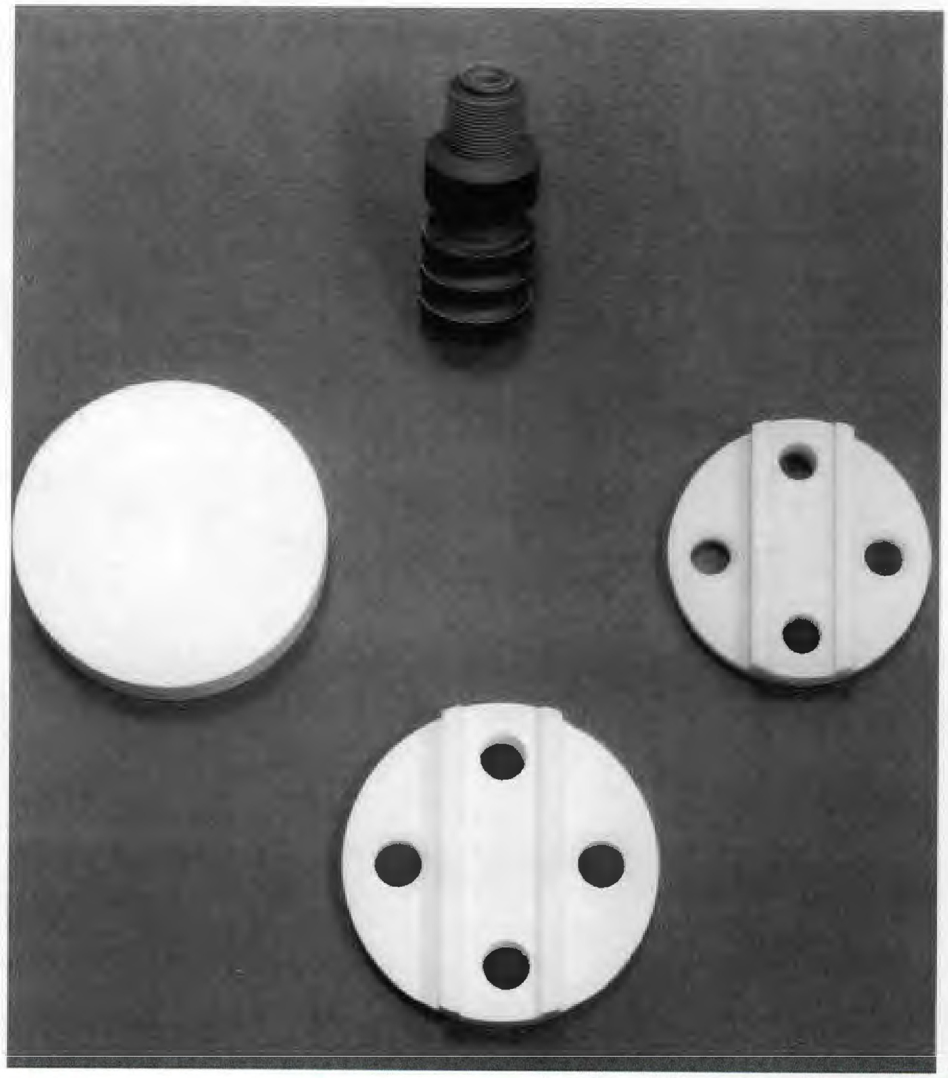


ORNL researchers recently produced green-machined parts from gelcast ceramic billets. From top counterclockwise are a silicon nitride part green-machined on a lathe and fired; a green gelcast alumina billet (55 mm in diameter); a green gelcast alumina disk after machining using a drill press and surface grinder; and a machined, gelcast alumina disk after firing.

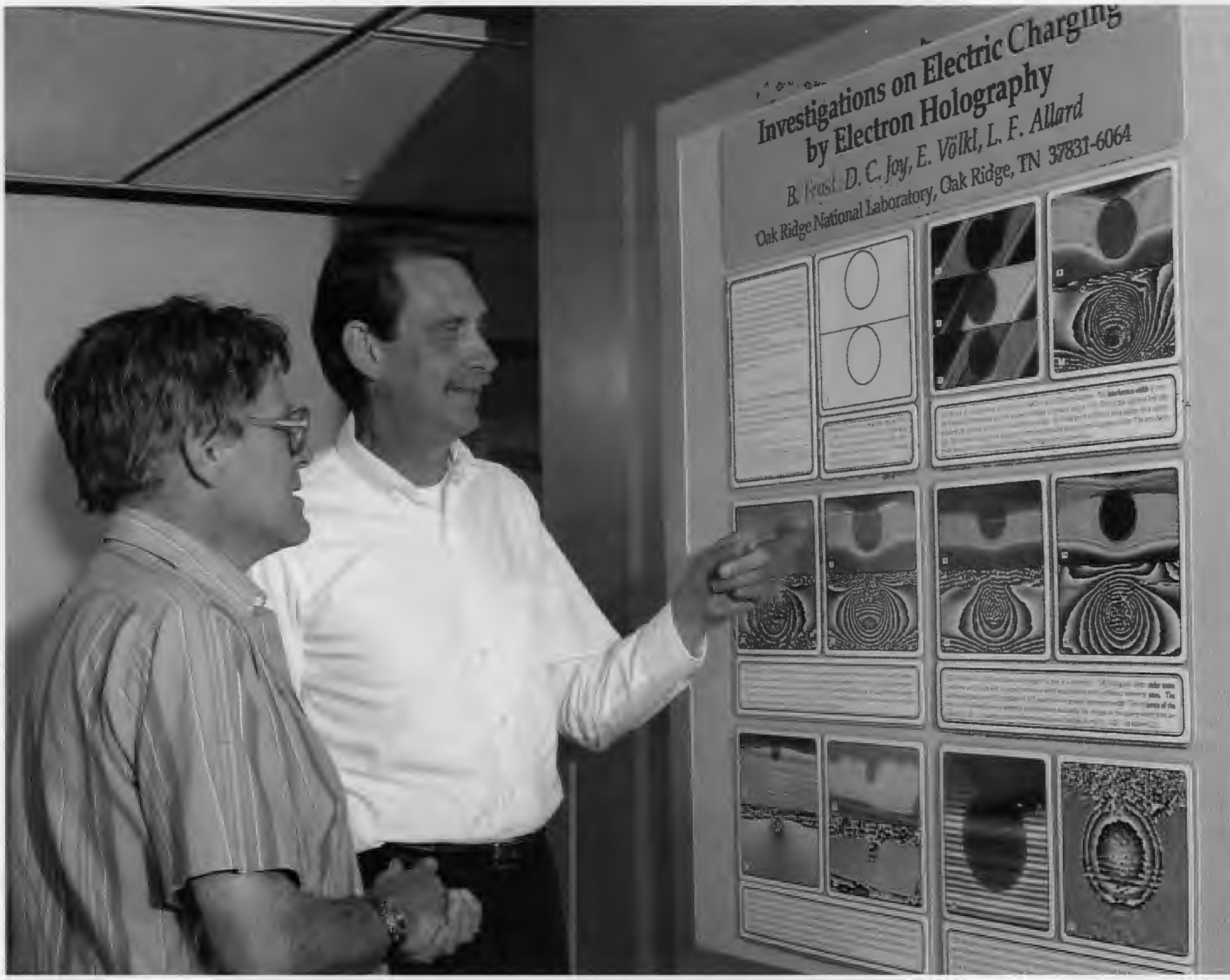
Larry Allard manipulates the controls of the Hitachi HF-2000 field emission transmission electron microscope.

Electron Holography: A New View of Material Structure

By Larry Allard, Ted Nolan, and David Joy

Holograms are familiar three-dimensional images seen in science museums, bookstores and specialty shops, and on magazine covers and credit cards. Each image is formed using specialized optical techniques and coherent visible light (typically from a laser) that illuminates the object of interest. The hologram, which is recorded on a photographic plate or on film, looks to the naked eye like a series of randomly sized, overlapping concentric circles. However, when the hologram is subsequently illuminated by an appropriate light source, a remarkable, three-dimensional (3-D) image appears within the plate. This image can be viewed from several angles, and parts of the object hidden when viewed from one direction come into view as the hologram is turned and viewed from another direction. ■ The optical hologram is formed by exposing the film simultaneously with coherent light that reflects from the surface of the object and by light that is split from the original illuminating beam and subsequently directed by mirrors so that it can overlap with the reflected beams as they are incident on the film. The interference pattern that is produced is directly related to the amplitudes (heights) of waves and phases (relative positions) of the waves reflected from the object. Because of the nature of this interference effect, 3-D information about the object is recorded in the hologram. By passing appropriately coherent illumination through the hologram, the imaging process is effectively reversed, and the object is "reconstructed." Changing the viewing direction relative to the plane of the hologram produces a continuum of differing reconstructions, and these appear as different views of the object.

ORNL has taken a leading role in electron holography.



David Joy (left) and Ted Nolan discuss Bernhard Frost's poster on holography of electric fields.

Father of Holography

In 1947 Dennis Gabor, a Hungarian-British physicist, proposed the method of interference imaging and gave it the name holography, from a Latin word meaning "whole writing." The father of holography did not envision its use as an optical technique, however, because he was an electron microscopist who wanted to find a way to sharpen images produced in transmission electron microscopes (TEMs), which were in their infancy in the 1940s.

An electron microscope produces a beam of high-energy electrons, using one of a variety of electron emitters in an "electron gun," and then directs the beam onto a thin specimen using electromagnetic lenses. The beam of electrons has the peculiar property that, because of the high speed of the electrons, it appears as if only one electron at a time is in the microscope and passes through the specimen. Thus, we consider not the particle properties of the electron beam, but the wave properties (moving particles have a wave nature according to quantum theory) in order to describe the formation of an image in the electron microscope. A

The goals of this project were to further develop and popularize electron holography internationally.

"plane wave" is presumed to be incident upon the top surface of the thin specimen, and the wave is modified by passing through the specimen to form an image. The resulting image is magnified as it is projected through several additional lenses, creating a final image that can be directly viewed on a fluorescent screen in the microscope or that can be recorded on photographic film or on a charge-coupled device (CCD) detector.

For specimens of crystalline materials, the regular arrays of atoms aligned on crystal planes can scatter, or diffract, the beam in different directions. The diffracted beams are recombined in the modern TEM to form a high-resolution image that gives details of the atomic structure of a crystal and imperfections in the arrangement of atoms in the crystal. However, the technology of the 1940s gave images with resolution too poor to reveal the atomic structure.

Gabor sought a method to remedy this situation. He realized that the TEM image, as with an image formed with any type of radiation, is simply a superposition of wavelets from each point in the thin specimen. The image varies in amplitude and phase from point to point, depending on the nature of the interaction between the incident beam and the specimen as the beam passes through the specimen. A recording medium such as film does not record these two image components separately, however. The intensities recorded are a combination of the amplitude and phase, which cannot be separated in any standard way.

Gabor knew that one of the primary lens aberrations in the TEM, the spherical aberration, affects the phase components of the electron beam. He reasoned that, if the phase component could be separated from the amplitude component, then perhaps the spherical aberration of the microscope could be corrected and eliminated from the image forming process. This change would inevitably lead to a marked improvement in the microscope's resolution. The primary problem was how to separate the image components.

One day, while waiting to begin a tennis match, Gabor had a brilliant flash of intuition. The path leading to the formal development of his method of holography became instantly clear to him. The essence of the method was the combination of two waves within the microscope: the incident, undeviated electron wave and the image wave, which exits the bottom surface of the thin specimen. If the electron optical geometry is correctly set up, these two waves can be made to interfere. The interference pattern then would be processed using optical techniques to form optical holograms.

After describing his method of recording images from which the amplitude and phase components could be separately extracted, Gabor encountered an obstacle when he tried to use the technique. The electron microscopes of his era did not produce an electron wave with sufficient coherence to permit the proper degree of interference required to make a useful hologram. Similarly, holograms could not be produced from ordinary light because typical light sources of the time produced beams that spread over large angles or had a wide range of wavelengths. Thus, holography did not become practical until the invention of the laser, which produces light of a single wavelength moving in one direction. Recently, the development of TEMs using highly coherent field-emission electron sources have made Gabor's original dream come true.

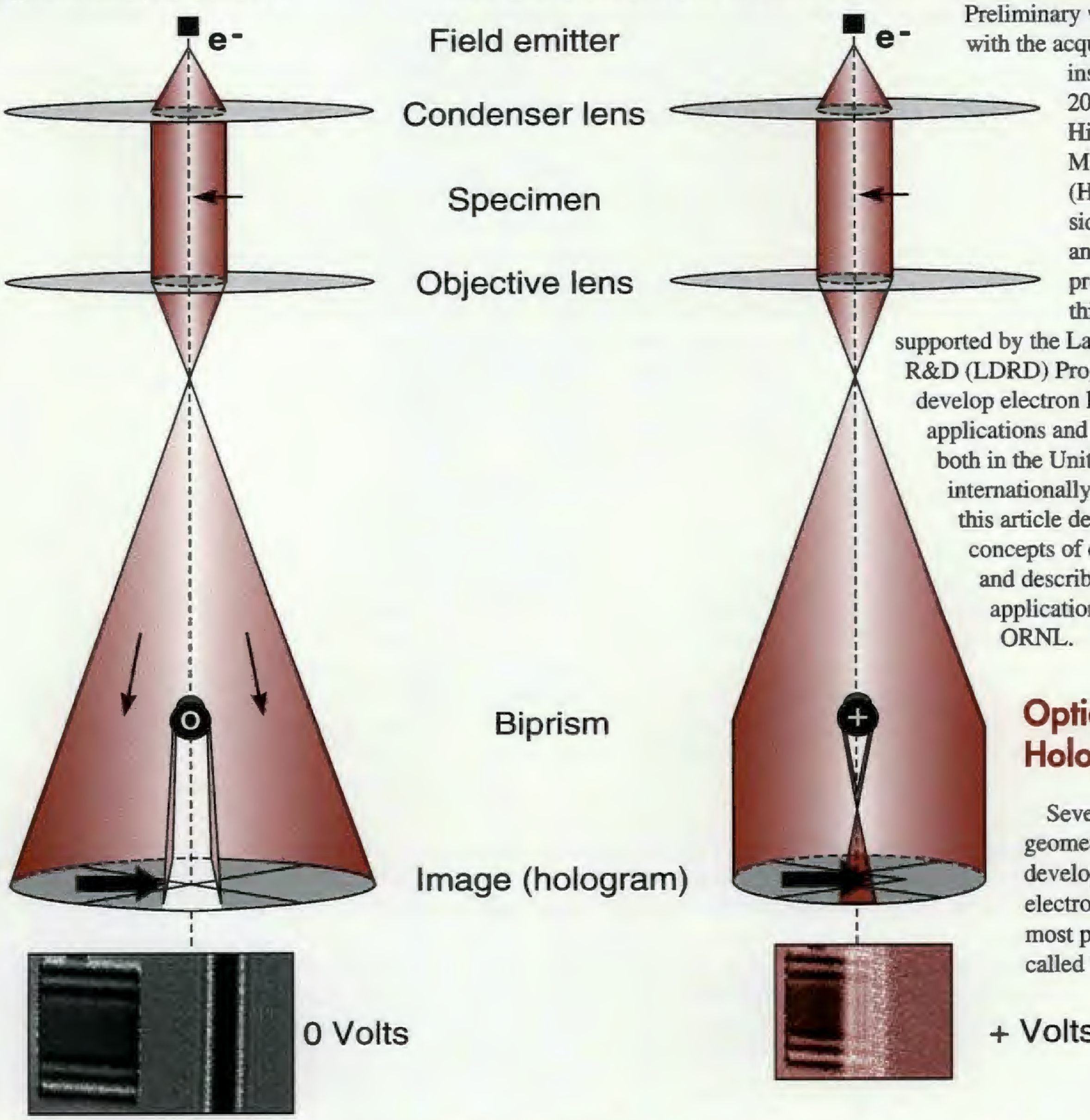
Electron Holography Comes to ORNL

After its invention, electron holography was advanced primarily by a group at the University of Tübingen, Germany, led by the work of Gottfried Möllenstedt, Heiner Düker, and Herbert Wahl, from the mid-1950s to the early 1970s. With the advent of lasers that produced coherent light beams, and the independent development of the technique of holography by Emmit Leith of the University of Michigan, optical holography was widely advanced and applied during this period.

Progress in developing electron holography techniques was slow for a number of years. Electron holography was not pursued strongly until the introduction of the field-emission electron gun on electron microscopes in the late 1970s. Holography at Tübingen was then carried on primarily by Hannes Lichte, who trained under Wahl and Möllenstedt. At the same time, Akira Tonomura from the Hitachi Corporation in Japan studied at Tübingen and returned to Hitachi to lead a major developmental effort in electron holography. Tonomura had the advantage of working for a company that manufactured electron microscopes, and he prodded Hitachi into developing the cold field-emission electron gun, which culminated in the construction of a 350-kilovolt (kV) instrument designed to be optimized for electron holography. This instrument is housed in the new Hitachi Advanced Research Laboratory in Hatoyama, Japan, a northern suburb of Tokyo. It was used for research conducted in a recently completed 5-year, $20-million program supported by the Japan Research Development Corporation. The program achieved its goal: it developed electron holography as a major technique for characterizing materials. As a result of Hitachi's introduction of a commercial 200-kV version of this instrument in 1989, followed by the introduction of 200-kV and 300-kV instruments by other manufacturers, the number of laboratories that can undertake electron holography has increased from only a couple to several dozen.

In the United States, Oak Ridge National Laboratory has taken a leading role in this field beginning in late 1990, when Hitachi installed their 200-kV HF-2000 TEM in the laboratory of David Joy at the University of Tennessee at Knoxville (UTK). Joy, an ORNL-UTK Distinguished Scientist, collaborated with Larry Allard and Ted Nolan, both of ORNL's Metals and Ceramics Division, in initiating electron holography research.

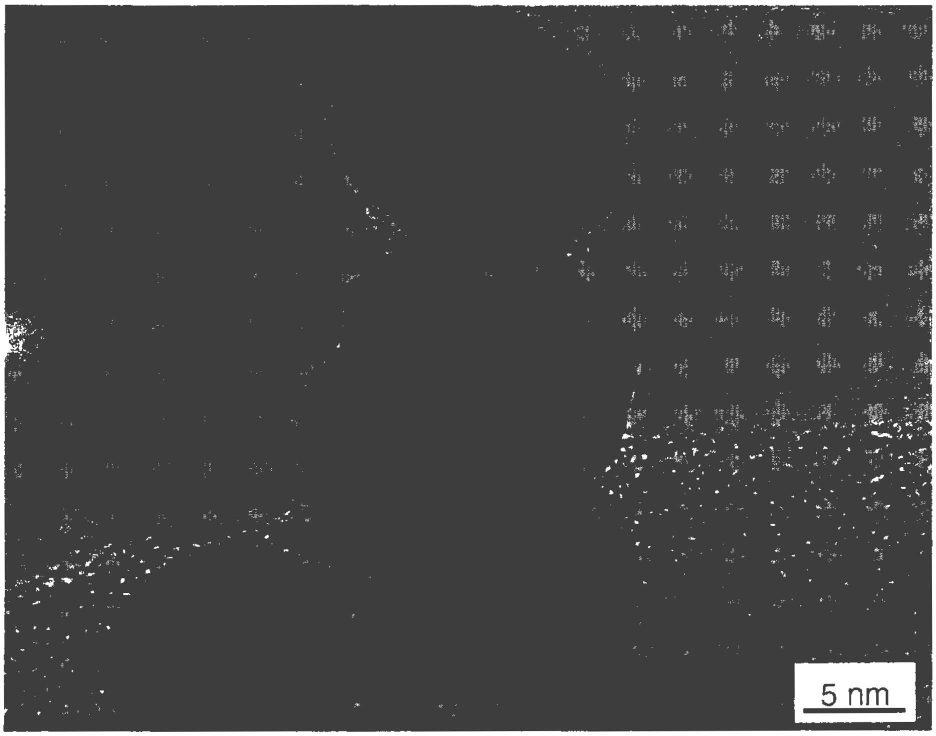
Preliminary work at UTK along with the acquisition and installation of an HF-2000 instrument in the High Temperature Materials Laboratory (HTML) at ORNL (see sidebar on p. 50) led to an internally funded project. The goals of this 3-year project supported by the Laboratory Directed R&D (LDRD) Program were to further develop electron holography applications and to popularize its use both in the United States and internationally. The remainder of this article details some of the basic concepts of electron holography and describes various holography applications pioneered at ORNL.



Geometry of electron holography: with no voltage on the biprism at left, waves from the object and reference do not overlap. A positive voltage on the biprism at right causes the waves to overlap, forming an interference pattern, or hologram.

Optics of Electron Holograms

Several electron optical geometries have been developed for making electron holograms, but the most popular one—the so-called "off-axis, image plane" geometry—is surprisingly simple, as illustrated in the figure at left. It employs the electron biprism,



Palladium nanocrystals sit on the surface of an amorphous silica sphere.

invented by Möllenstedt and Düker in 1955. This device is simply an ultrafine (0.3 micrometers in diameter) conductive fiber positioned in an imaging lens perpendicular to the electron beam so that it splits the field of view (left). A thin TEM specimen is placed over one side of the image field. When a positive voltage is applied to the fiber, the electron waves on either side of the fiber are bent toward the center, eventually causing them to overlap (right). The overlapping waves create an interference pattern of parallel fringes. These fringes are changed in position and contrast, depending upon how the specimen affects the electron beam. The pattern is recorded either on film, or in the case of the ORNL instrument, directly onto a digital CCD camera system. This interferogram, or hologram, is then processed to yield separate amplitude and phase images.

The digital processing software package currently in use in our laboratory was written by Edgar Völkl, who came to ORNL from the University of Tübingen as part of his postdoctoral assignment for the LDRD project. This powerful, sophisticated, easy-to-use Macintosh software package (called HoloWorks™) has recently been licensed for commercial sale by Gatan, Inc., the manufacturer of the digital camera system used on the HF-2000. It is in use in several laboratories in Europe and Japan, as well as in the United States.

In addition to providing a multifaceted hologram-processing software package, our electron holography project at ORNL also has pioneered applications of holography in a variety of materials science areas.

ORNL Applications of Electron Holography

Shapes of nanocrystals. The technique of electron holography offers a unique capability to characterize the three-dimensional structure of nano-sized crystals—crystals about a hundred-thousandth of a millimeter in diameter. We have used this technique (as described below) to study (1) nanocrystals of palladium supported on silica microspheres to simulate a catalyst material (see figure at left), and (2) shapes of nanocrystals of zirconium oxide (zirconia) to determine effects of particle shape on the behavior of the material during sintering.

Catalytic materials are typically composed of metallic nanocrystals that are supported on a highly porous material such as aluminum oxide. Such materials are used to control emissions from automobile exhaust and refine crude oil to produce gasoline. The morphology of these nanocrystals is of great interest to catalysis chemists because morphology (i.e., the nature of exposed crystal facets, or sides) affects the behavior and performance of the catalyst.

Although high-resolution TEM techniques have made it possible to image nanometer-sized particles at atomic resolution, extracting details of structure and morphology on an atomic scale is still a formidable challenge. The oxide support of a metal catalyst often obscures details of the morphology of such particles. One way to circumvent the problem of studying finely dispersed supported metal particles is to use a model support of simple geometry such as amorphous silica microspheres. This model structure permits metal particles deposited on the surface to be observed looking essentially parallel to the plane of contact between the particle and the

We have reported the first observations of nano-scale voids in metallic single-crystal particles.

sphere. The particle that protrudes from the edge of the sphere (see figure below) provides information on particle morphologies and interface structures. This geometry is also ideal for the formation of electron holograms from which pure phase images can be reconstructed.

Professor Abhaya Datye, our colleague from the University of New Mexico, provides a model catalyst specimen consisting of fine palladium (Pd) nanocrystals that were deposited on amorphous silica microspheres 0.2 micrometers in diameter. The Pd particles were roughly spherical, often faceted, single crystals, as shown in the figure on p. 43. Most Pd nanocrystals exhibited a central contrast feature, also often faceted, that typically extended over one-third the diameter of the particle. This feature was presumed to be an internal void, because the crystal lattice planes always extended through the feature, and no feature was ever observed intersecting with the particle surface. However, it cannot be determined from the direct TEM image whether the void is empty or filled with an amorphous material.

An electron hologram of a single Pd particle on the edge of the silica microsphere is shown at top right. The reconstructed phase image appears at the bottom of p. 45. To analyze the phase image, we recognize that the intensity at any point in the phase image represents the change in phase of the electron wave front with respect to the reference wave. This phase change is directly proportional to the local thickness of the material through which the electron beam is passing, if the sample material is uniform in composition and very thin, as is the case for the Pd particles discussed here. Thus, any changes in the intensity of the phase image can be directly ascribed to variations in sample thickness.

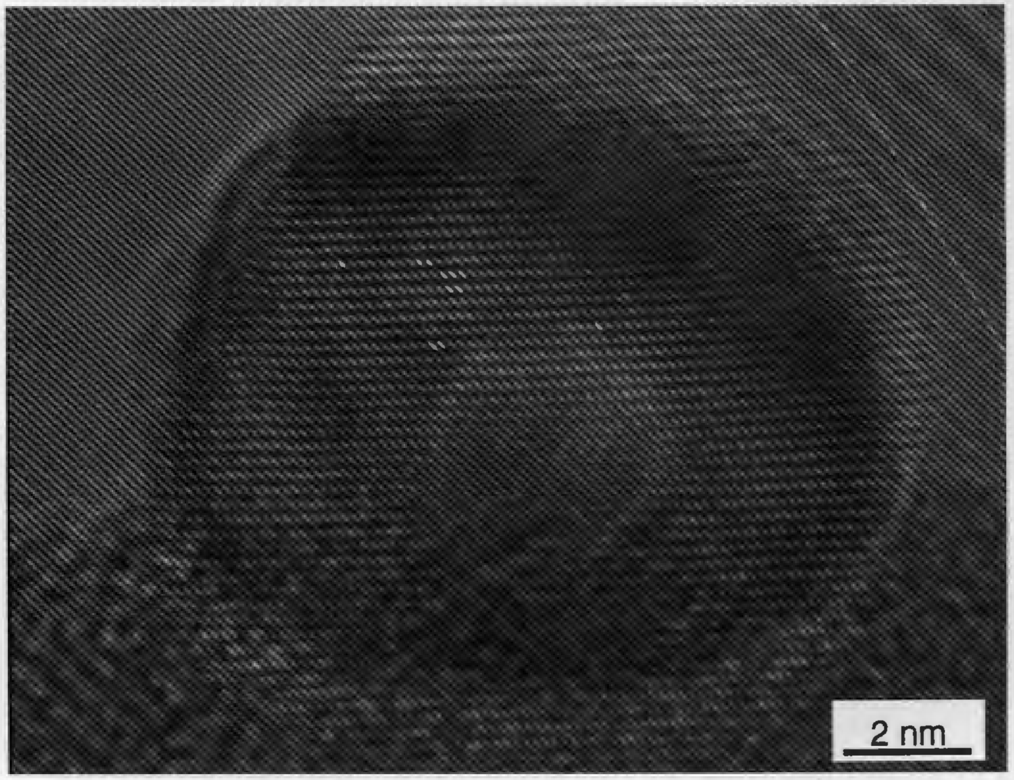
The change in phase from point to point across the particle along the line shown (i.e., the phase profile) is shown in the figure at the bottom of this page. Using the geometry of the actual particle (assumed to be spherical) and assuming a spherical void slightly offset from center as shown, the expected phase profile was computed (thick gray line). The excellent match of the experimental phase profile with the computed phase profile is convincing evidence that the Pd particles actually contain voids.

To the best of our knowledge, we have reported the first observations of nano-scale voids in metallic single-crystal particles and have made the first unambiguous determination of a void structure in any material.

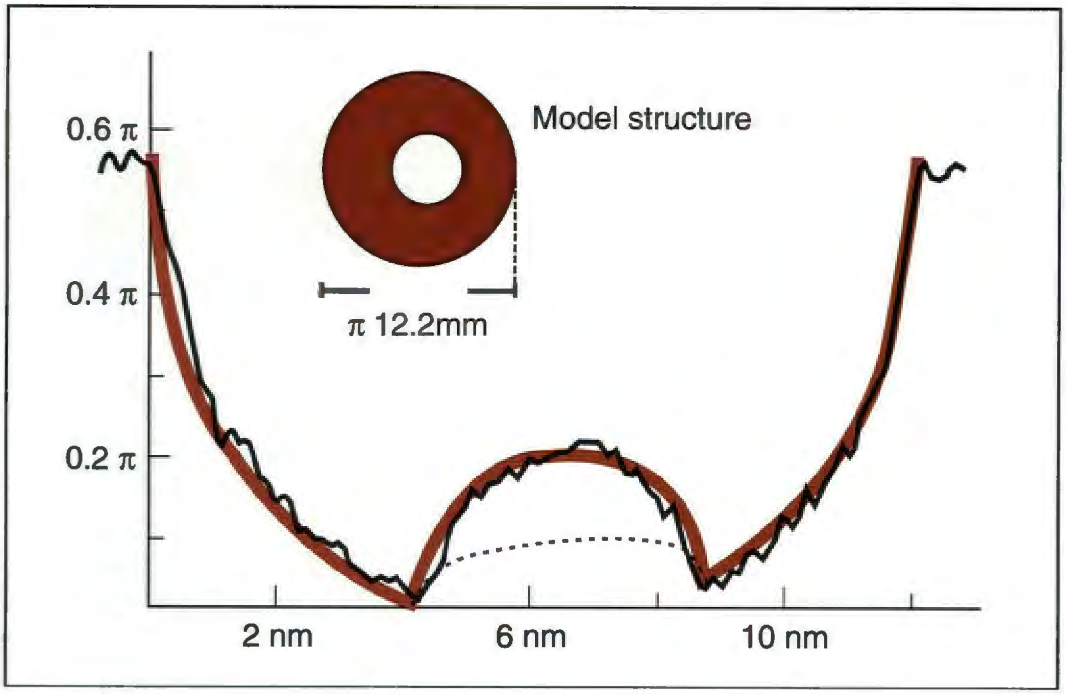
Professor Altaf Carina of Pennsylvania State University is studying the mechanisms of sintering of fine ceramic powders such as zirconium oxide.

Nanocrystalline zirconia (ZrO_2) particles often exhibit faceting—they have flat sides like larger crystals—and thus appear to be polyhedral (many-sided) from high-resolution images. However, the actual shapes of such particles have not previously been determined. The material has a cubic

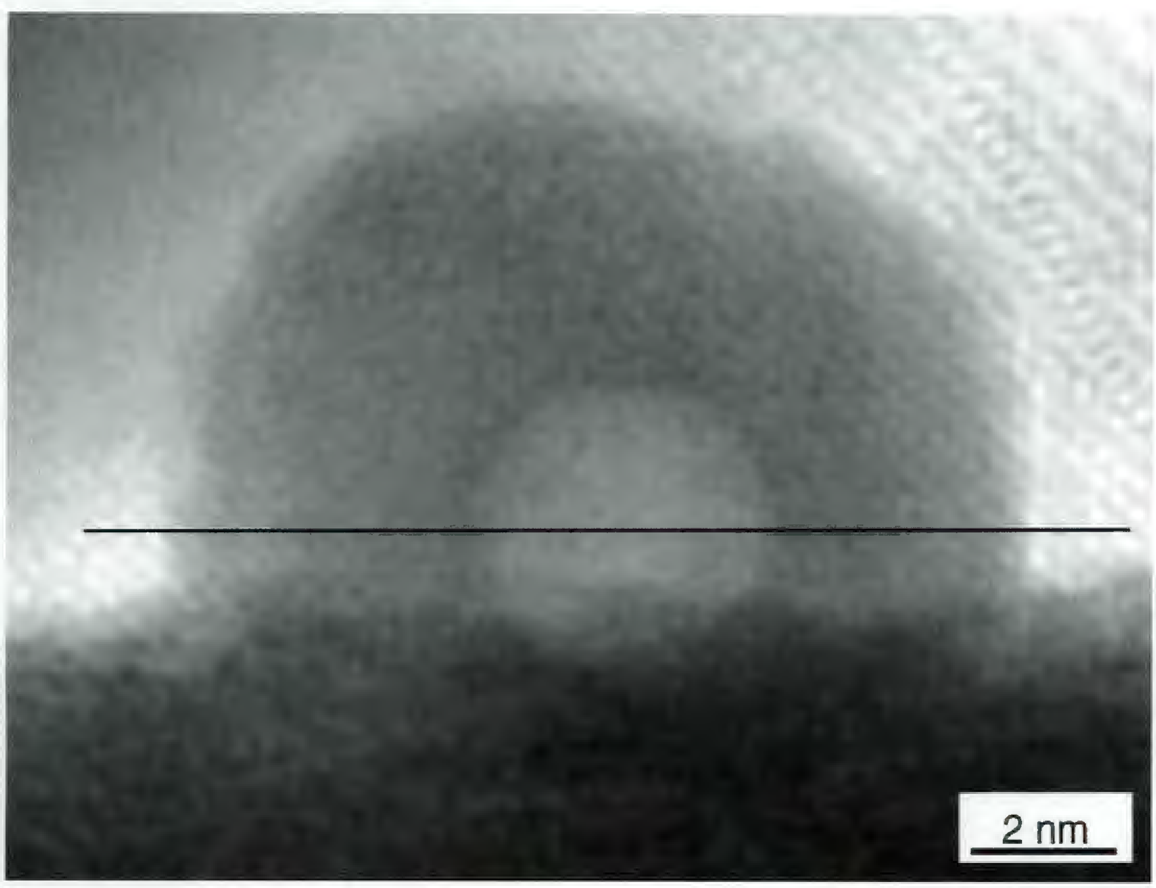
continued on p. 46.



Electron hologram of a single palladium nanocrystal at the edge of the silica sphere.



Comparison of the experimental (black line) and calculated (gray line) phase profiles. The close match confirms the presence of a void in the particle.



A phase image is reconstructed from the hologram, showing line for phase profile.

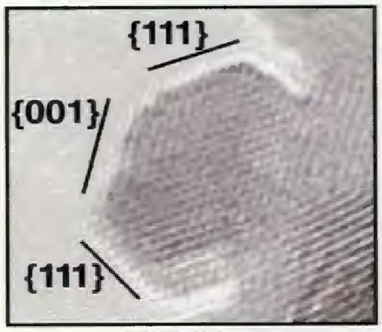


Fig. A
A high-resolution image of a zirconia nanocrystal.

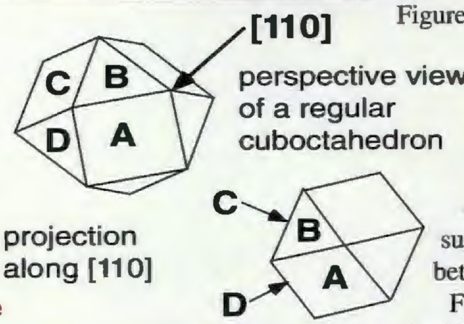


Fig. B
A perspective view of the expected cuboctahedral shape of the crystal, and a view (right) looking down the crystal direction corresponding to the image of Fig. A.

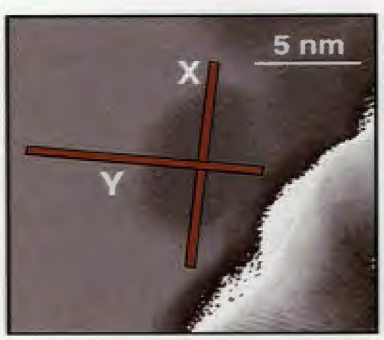
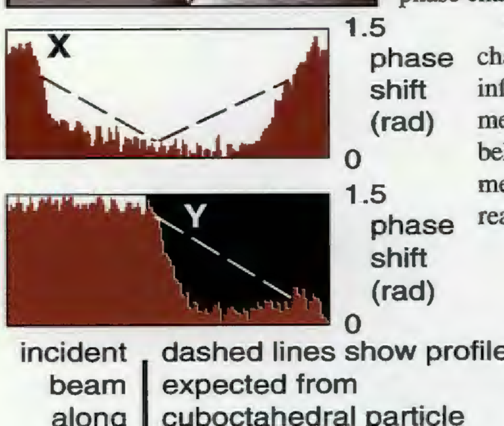


Fig. C
Phase image showing lines X and Y for two phase profiles.



Figs. D and E
The phase profiles correspond to lines X and Y. The dotted lines show profiles expected from the cuboctahedral crystal.

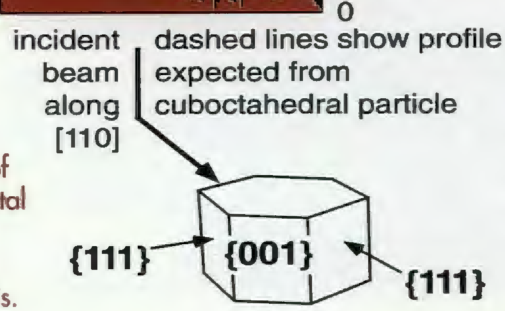


Fig. F
A perspective view of the shape of the crystal (a right prism), as suggested by the phase image analysis.

Any changes in the intensity of the phase image can be directly ascribed to variations in sample thickness.

crystal structure, and the apparent surface-bounding planes generally lie along cube faces and cube diagonals (which make octahedra, or eight-sided shapes), so it is natural to assume they have a shape. Figure A shows a high-resolution TEM image of a nanocrystalline zirconia particle, and Fig. C shows the corresponding phase image. Analysis of the high-resolution image of the particle suggests that it is viewed looking perpendicular to one of the cube edges in the basic crystal structure. The particle appears to be cuboctahedral based on the bounding planes and overall projected shape. The relative lengths of the facets suggest a polyhedral morphology approximately halfway between an octahedron and a cube.

Figure B shows a sketch of the projection of a cuboctahedron looking in the same crystal direction as the particle is viewed, showing the correspondence between the particle and the model. The line profiles (Figs. D and E) through the phase image, however, are not consistent with the anticipated particle shape. If the particle were cuboctahedral, the profile along line X would show a continuous, linear change in phase, for example, as indicated by the dotted line in Fig. D. The abrupt phase change actually seen, coupled with a region of essentially flat phase seen in both the X and Y profiles, suggests that the particle is a "right prism" rather than a cuboctahedron. A sketch of the prism, which satisfies the experimentally observed phase changes, is shown in Fig. F.

Clearly, electron holography is a useful technique for characterizing shapes of nanoparticles. This type of information should prove invaluable in better understanding mechanisms of sintering in nanostructural ceramics and the behavior of catalysts that have similar-sized particles of heavy metals, which serve as the primary structures that initiate reactions.

Ferroelectrics. Ferroelectrics are materials that exhibit spontaneous electrical polarization, analogous to the way in which ferromagnetic materials show spontaneous magnetism. Spontaneous electrical polarization refers to pairs of separated positive and negative charges, each like a needle on a compass. When an electric field is applied, the polarization may change, just as when you turn from facing north to facing south while holding a compass and the needle shifts to point in the opposite direction. Because ferroelectric materials can both respond to and generate electric fields, they are important as potential information storage media, sensors and actuators, and light waveguides. They are a member of the class of "smart" materials identified as being of significant technological importance.

Although ferroelectrics have been studied quite intensively, the details of their electric domain structures—randomly oriented regions of uniform electrical polarization—have remained unclear because of the practical problems associated with imaging the domains and domain walls. Conventional diffraction techniques in the transmission electron microscope produce only weak contrast between regions of different polarization. This deficiency results from mechanical strain caused by the polarization rather than by the electric field itself. As a consequence, it was not known how wide the walls were between domains nor how the polarization rotated across the wall—parameters that play an important role in determining the behavior of the ferroelectric material.

Electron holography provides a solution to these problems. We have demonstrated its capability in our studies of barium titanate ($BaTiO_3$), a ferroelectric material. As the electron wave transmits through the ferroelectric material, its phase is altered by the polarization of the material, because the phase is influenced in different ways by the varying directions of the electric potential in the

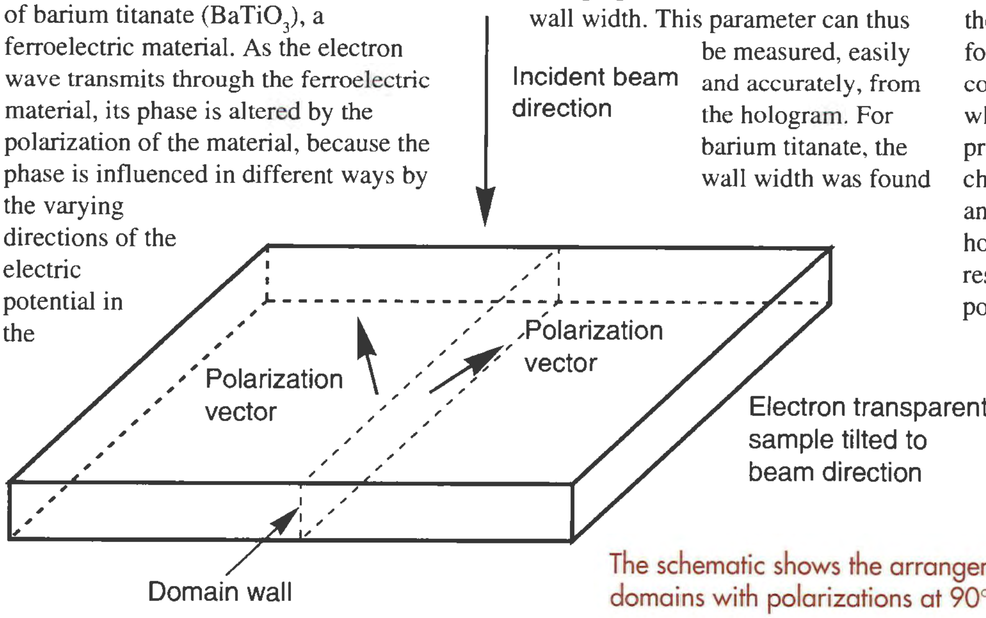
We have studied the behavior of ferroelectrics exposed to increasingly high temperatures.

ferroelectric domains. This phase change from area to area in the specimen can be measured directly from the hologram.The figure below shows schematically the arrangement used for observation. Two domains with polarizations at 90° to each other are separated by a domain wall. The specimen is tilted so that some component of the polarization is parallel, or antiparallel, to the beam direction, and the sample is thin enough so that electrons can be transmitted through it.

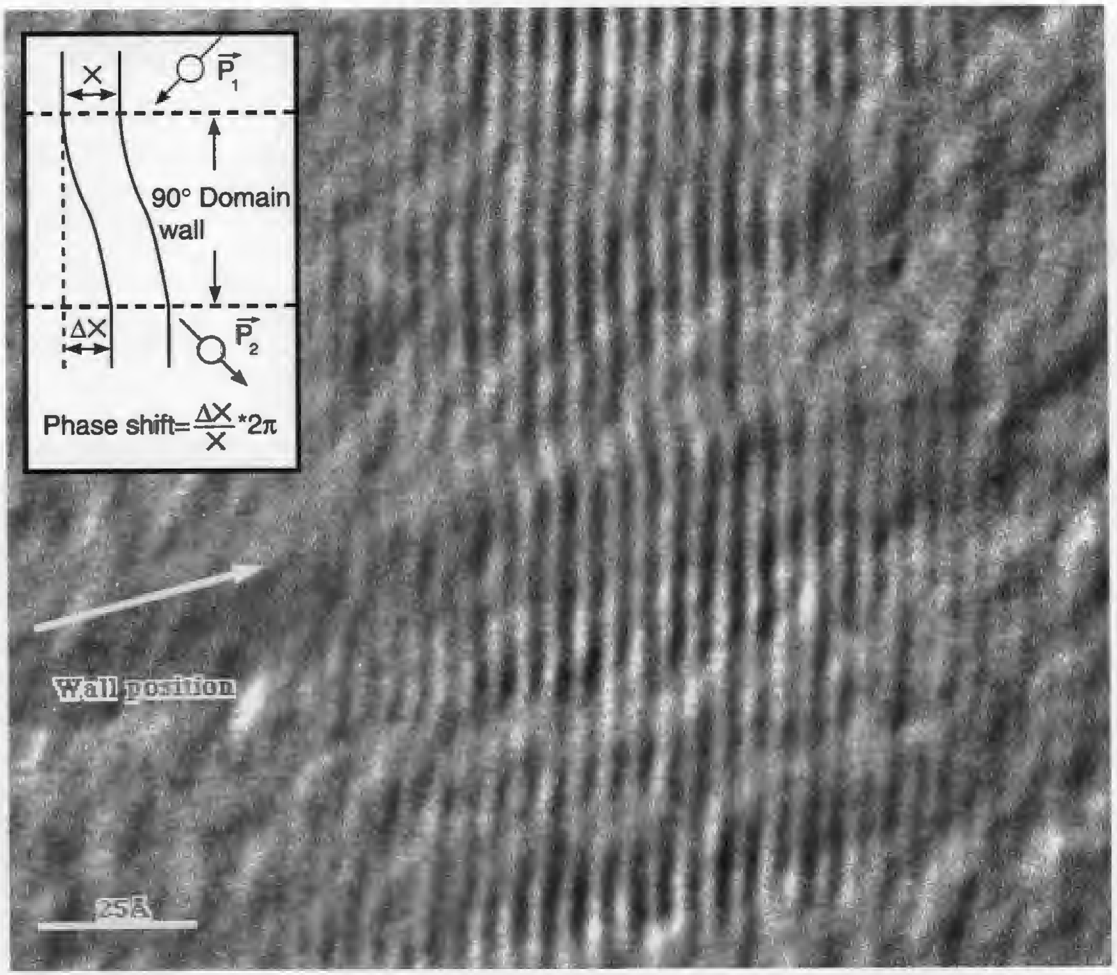
The figure on p. 48 shows the hologram recorded from such an area. Note that, as the fringes in the hologram cross the position of the domain wall, they shift sideways. Each fringe represents a contour of constant phase so the lateral shift shows that the phase experienced by the transmitted electron waves changes as they cross the domain wall. The distance over which this change occurs, measured perpendicular to the domain wall, is the range over which the polarization is changing and is, therefore, the domain wall width. This parameter can thus be measured, easily and accurately, from the hologram. For barium titanate, the wall width was found to be between 2 and 5 nanometers (nm), in good agreement with the most recent theoretical estimates but nearly a factor of 10 smaller than earlier experimental measurements made using standard diffraction contrast imaging methods.

The exact way in which the polarization vector rotates from one side of the domain wall to the other can also be derived from the fringe bending shown in the figure on p. 48 because the extent of the lateral shift is proportional to the component of the polarization parallel to the beam direction. The insert in the figure shows how the phase shift across the domain boundary can easily be measured.

We have used the same experimental method to study a variety of other ferroelectric materials and to investigate the behavior of ferroelectrics exposed to increasingly high temperatures. Subjecting the material to increasing temperature destroys the domain structure. The domain structure reforms as the temperature is lowered. We have found that the previous domain configuration usually is "remembered" when the domains reform, indicating the presence of defects and other characteristics that control domain size and location. An analysis of the electron holograms indicates that the defects responsible for this memory are probably positions in the crystal lattice where oxygen atoms are missing, resulting in a buildup of electrons, or "charged oxygen vacancies." This solution had been predicted theoretically, and our work provided the first supporting experimental observations.



The schematic shows the arrangement of ferroelectric domains with polarizations at 90° to each other.



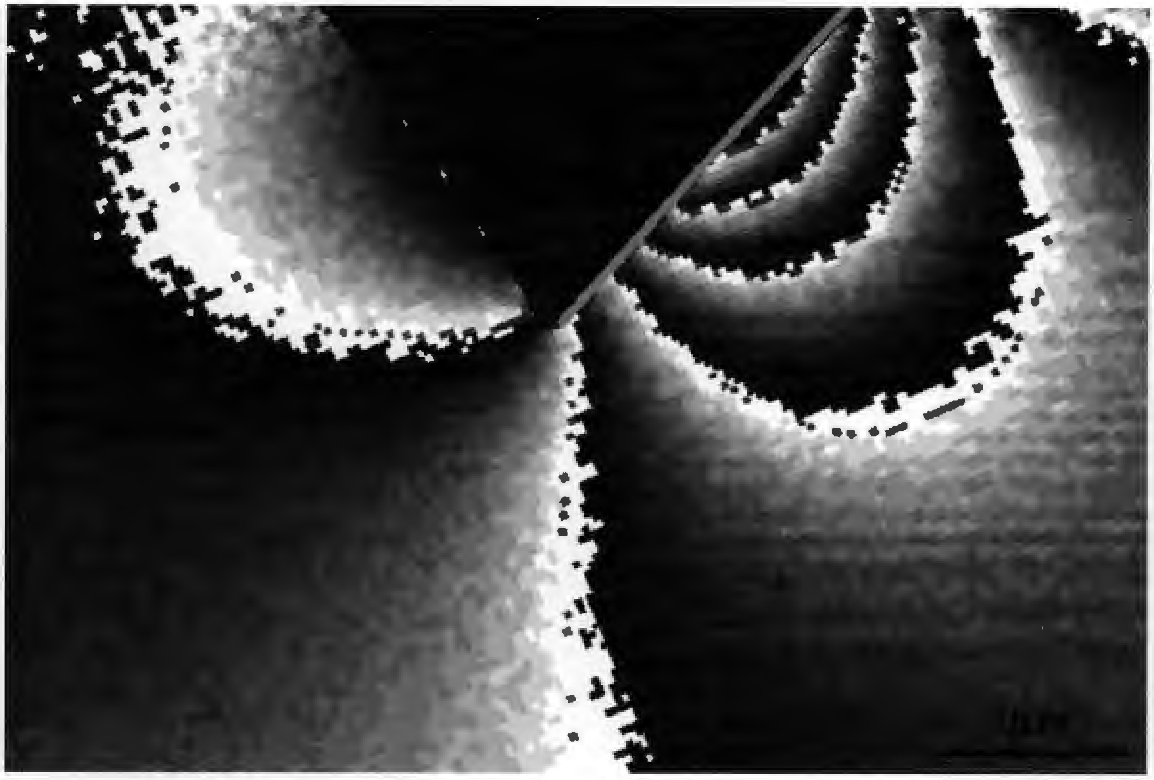
The hologram recorded across a domain boundary clearly shows the fringe bending that results from the different polarizations. The inset shows the relationship between the degree of fringe bending and phase shift.

We have found that the previous domain configuration usually is "remembered" when the domains reform.

Magnetic Field Measurements. With the advent of the new technique of magnetic force microscopy (MFM), surface magnetic field effects in different regions (domains) of a magnetic material can now be imaged at the micrometer level of resolution. In this special technique, which is related to atomic force microscopy (AFM), a sample is scanned in a raster pattern by a special AFM probe having a sharp tip, and the magnetic forces between probe and sample are monitored. However, to interpret quantitatively the magnetization effects in magnetic domains, both the field distribution around the tip apex and the separation between the tip and the sample must be known exactly. Bernhard Frost of the University of Tennessee has developed new holography techniques to image these magnetic fields.

The magnetic probe shown at the bottom of p. 49 is a commercially available pyramid-shaped piece of silicon nitride positioned at the end of a cantilever. The cantilever attaches to an AFM, which provides the raster motion of the tip over the specimen. Prior to use the tip is coated with about a 100-nm-thick film of a magnetic material such as nickel-cobalt (NiCo) on the front face. After deposition of the magnetic layer, the probe is magnetized by applying an external field along the pyramid axis.

The figure at the top of p. 49 is a phase image reconstructed from a hologram of the projected side view of the tip, which appears as the black triangle. This view looks edge-on to the magnetic layer, which is indicated schematically by the thin gray line that has been superimposed on the right-hand edge of the tip. The magnetic lines of force surrounding the tip have been made visible in this reconstruction, because the phase of an electron wave is sensitive to magnetic fields. The total "flux," or amount of



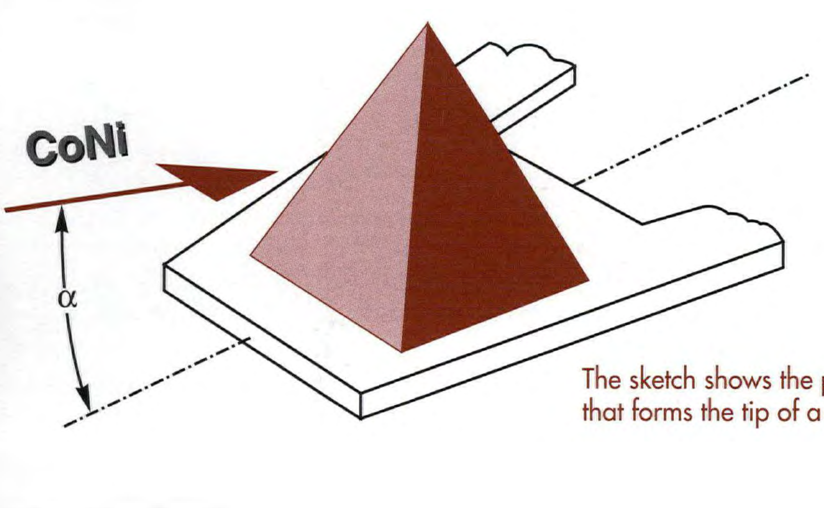
The phase image from the MFM tip. The view shows the tip in profile, and phase lines represent the magnetic lines of force emanating from the magnetic layer deposited on one face of the tip (thin gray line on right-hand edge).

Electron holography will rapidly become a standard technique in materials characterization.

magnetic field affecting the sample over a specific area imaged in an MFM, can be determined by the number of black lines revealed in the phase image, because the magnetic flux between two succesive black lines is known. For example, in one experiment at a working distance of 100 nanometers, we found the total magnetic flux over an area of 1 micron by 1 micron to be 6 millitesla. The magnetic field directly under the tip was 36 oersteds, while at a position 500 nm away laterally from this point to the right, the magnetic field was 26 oersteds. The shape and the strength of the field surrounding the tip are important quantities that govern the performance of the MFM. The use of electron holography for the first time to characterize these MFM tips now permits us to quantify the nature of the magnetic field effects around the tip. In this way, we can better quantify the magnetic domain images obtained when the MFM tip scans a magnetic specimen.

Conclusion

We have presented here only a few of the many uses of electron holography to provide new and unique information about materials structures and properties. As we gain further experience in the art of electron holography, we find that the technique can be applied to almost every specimen type that we observe in our laboratory. It is indeed gratifying that our work has gained significant recognition in the field, so that many well-known researchers in the field, including some from international laboratories, have come to work with us. As increasing numbers of the new generation of field-emission electron microscopes become available, we expect that many laboratories will offer this capability in the future and that electron holography will rapidly become a standard technique in materials characterization. **ornl**



The sketch shows the pyramid-shaped piece of silicon nitride that forms the tip of a magnetic force microscopy cantilever.

The HF-2000 Cold Field-Emission Electron Microscope

Bernhard Frost (front) and Edgar Völkl collect electron holograms at the HF-2000 cold field-emission electron microscope.

The HF-2000 cold field-emission electron microscope is a hot new item in ORNL's High Temperature Materials Laboratory (HTML). Users at the the Materials Analysis User Center in the HTML like its remarkable capabilities. So do its sponsors in DOE's Office of Transportation Technologies, which reports to the Assistant Secretary for Energy Efficiency and Renewable Energy.

This instrument is the culmination of two decades of development by Hitachi Ltd., in Japan. It is the only transmission electron microscope currently available that operates at 200,000 volts and uses cold field- emission technology. "Cold field" refers to the fact that the filament in the instrument's electron gun operates at room temperature, limiting the energy spread of the electron beam to about 0.5 electron volts. Such a low energy spread coupled with the small diameter of the electron source generates the highly coherent beam needed for recording high-quality electron holograms.

This microscope is the only commercial instrument that is constructed using expensive Permalloy housings for the electromagnetic lenses. Permalloy construction provides extra shielding against the effects of external magnetic fields, which can distort images and degrade holograms. It has an advanced dry-pumped vacuum system designed partly to our specifications, eliminating the possibility of contamination of the inside of the microscope with oil vapors from standard vacuum pumps.

Another feature of this microscope is the high electron current available in the finest beam sizes (e.g., 1 nanoamp current in a beam 1 nanometer in diameter). This fine probe can generate

X rays from nanometer-sized areas of the specimen. The X rays, which are detected using a solid-state detector system mounted on the microscope, have energies characteristic of the particular elements present in the irradiated microarea. A spectrum of these energies is displayed directly on an Apple Macintosh computer, allowing rapid correlation of specimen features with the elements they contain.

The HF-2000 is also equipped with a digital camera system from Gatan, Inc. The camera operates with a charge-coupled device (CCD) chip, similar to the technology used in modern camcorders (except that our camera system cost $100,000). The CCD camera records images up to 1000×1000 pixels (picture elements) in size, giving us the advantage of immediate viewing, processing, and analysis of images as well as rapid hard-copy output. This system offers greatly enhanced data collection for this instrument as well as for all the other electron microscopes in our laboratory that are equipped with digital recording devices. Most important, the digital camera eliminates film handling and associated chemical wastes of old-fashioned electron microscopy.

A newly developed spectrometer system, now being installed, will permit digital images to be made from electrons that have lost specific amounts of energy as they pass through the specimen. This "imaging filter," also provided by Gatan, Inc., fits below the microscope and accepts the electron beam into a magnet that bends the beam around into a detector. The electrons that lose energy are bent through a greater angle, enabling them to be selected appropriately by a slit system and used to form the "energy loss image." With the low energy spread of the cold field emitter, we expect to be able to generate images that will show, for example, the dispersion of nanocrystals of diamond, the crystalline form of carbon, on an amorphous carbon film. These "maps" of the locations of elements can be generated with just a few seconds' exposure at nearly the resolution of the standard microscope image.

Operators in other cities can control our microscope, right from their lab computer.

The digital imaging capabilities available on the HF-2000 electron microscope have opened a new and exciting possibility for extending the usefulness of the instrument and for improving the quality and quantity of our research results. We have developed both an interface to the microscope and software that is integrated into the camera control software, allowing an operator to control the microscope to a large extent directly through the local computer. This control capability has been extended to allow operators in other cities to have the same control, right from the computer in their own office or laboratory. An inexpensive (about $200) commercial remote operation program called TimbuktuPro and a small digital camera such as the Connectix QuickCam (about $90) permit remote users to access the local microscope and see its display on their terminals. Each user also can communicate in a "TelePresence" mode with local operators via the QuickCam camera system, much like scattered participants in a teleconference who "see" each other on a computer screen. When the remote user operates the computer mouse, the same motion springs up on the local computer, thus providing all of the microscope control functions directly to the remote user.

A number of demonstrations of the remote operation of our HF-2000 have already been conducted, from locations such as San Diego, Washington, Nashville, and Detroit. Many industrial and university users are already excited about the possibility of interacting with us on a more frequent and timely basis. In many instances, this capability will eliminate the need to travel long distances to complete research, saving time and money.

International Workshop on Electron Holography

One of the missions of ORNL's LDRD electron holography project was to popularize the use of electron holography for materials and biological science research.

One of the missions of ORNL's LDRD electron holography project was to promote and popularize the use of electron holography for materials and biological science research. In addition to developing new techniques and applications and publishing the results of the research, ORNL researchers organized three international symposia/workshops, which were sponsored by the project. The first symposium, which was held in June 1992 in Knoxville, Tennessee, focused on coherent beam microscopy techniques, including electron holography. The second was a 2-day symposium on coherent beam imaging and digital microscopy; it was held in conjunction with the Microscopy Society of America (MSA) meeting in August 1993 in Cincinnati. Papers from this symposium were subsequently published in 1994 as a special issue of the MSA *Bulletin*.

The third and most significant workshop was co-sponsored with the Tonomura Electron Wavefront project in the Experimental Research for Advanced Technology Program of the Japan Research Development Corporation (JRDC). The Japanese government provided $20 million for this 5-year program of research in electron holography, which was directed by Akira Tonomura of the Hitachi Advanced Research Laboratory, one of Japan's leading candidates for the Nobel Prize for physics. Most of the funding for the workshop was provided by the Japanese government through the JRDC, which wanted to publicize further the outstanding results obtained during the run of the Tonomura project. Because of the recognition achieved by the ORNL project during its brief run, the JRDC management decided that a joint workshop held in the United States would be the best way to celebrate the end of both holography projects. The 3-day workshop was held in August 1994, also in Knoxville. It had nearly 30 invited speakers, including 18 from overseas.

More than 35 full papers were published as a hardbound proceedings from this workshop by Elsevier North-Holland. Two of the five editors of this book, *Electron Holography*, are associated with ORNL—Larry Allard of the Metals and Ceramics Division and David Joy, ORNL-UTK Distinguished Scientist.

BIOGRAPHICAL Sketches

LARRY ALLARD is a senior research staff member in the High Temperature Materials Laboratory (HTML) of ORNL's Metals and Ceramics Division. He holds B.S.E., M.S.E., and Ph.D. degrees in materials science and engineering from the University of Michigan. While at the University of Michigan for 13 years, he co-founded the Electron Microbeam Analysis Laboratory and served for several years as group leader and associate director. In 1986 he joined ORNL as a member of the HTML's Materials Analysis User Center, where he has used various electron microscope techniques to study ceramic whiskers, structural ceramics, ceramic-matrix and metal-matrix composites, and catalysts. In recent years he has co-organized four symposia or workshops in holography and coherent beam imaging, and he is currently co-organizing the 2nd International Holography Workshop as well as a workshop on Direct Imaging of Catalytic Materials. He is a recent recipient of a Lockheed Martin Energy Systems Technical Achievement award, and he is co-editing with David Joy and Edgar Völkl a new textbook on electron holography.

TED NOLAN, a senior research staff member in ORNL's Metals and Ceramics Division, is manager of the division's Materials Analysis Group in the High Temperature Materials Laboratory. He holds degrees from Purdue University and the University of Louisville and has undertaken advanced studies at the University of Tennessee at Knoxville. He was one of the first staff members to join the team that created the HTML User Program. His research at the HTML has focused on studies of high-temperature structural ceramics, ceramic whisker growth, ceramic composite interfaces, and catalysts. More recently, he has been instrumental in implementing digital imaging and data analysis in the Materials Analysis Group, which is now a national leader in digital microscopy. Before coming to ORNL, Nolan spent many years characterizing materials systems for gaseous diffusion and advanced uranium isotope separation processes at the Oak Ridge K-25 Site. He is a recent recipient of two Lockheed Martin Energy Systems technical achievement awards and a best paper award.

DAVID JOY is a University of Tennessee–ORNL Distinguished Scientist. He has an M.A. degree in physics from Trinity College, Cambridge University, and a D.Phil. degree in materials science from the University of Oxford. After 13 years at AT&T Bell Laboratories in New Jersey, he joined the staffs of ORNL and the University of Tennessee at Knoxville in 1987. Since that time, he has been involved in the development of electron holography and other advanced microscopy and microanalytical techniques. Joy is the author or co-author of more than 200 publications in electron microscopy and the author or editor of 7 books. He is past president of the Microbeam Analysis Society of America and winner of the Microscopy Society of America Burton Award for Early Achievement.

Materials Under Stress: ORNL's Measures for Helping Industry

By Carolyn Krause

Cam Hubbard at an X-ray diffraction instrument at ORNL's Residual Stress User Center.

When metal alloys, ceramics, and composites are shaped into objects such as components for automotive and diesel engines, they go through "manufacturing boot camp." These materials may be subjected to bending, rolling, twisting, pulling, pressing, heating, cooling, casting, forging, and joining to produce desired shapes. And that's not all. The objects are then finished through machining, grinding, and coating. As with other manufactured objects put into "operational combat," when the car or truck accelerates, its components are subjected to rapid changes in temperature and other forces that may cause deformation. ■ As a result of these manufacturing steps and numerous forces, "residual" internal stresses will develop in the structural materials. Residual stresses are defined as "stresses that remain in the absence of any applied external forces." These residual stresses must balance over the part—negative (compressive) in one region and positive (tensile) in another. ■ A residual stress can be a problem waiting to happen. When you bend a metallic part, it may not break the first time. However, residual stresses in the part may have developed. The next time it is bent, more stresses may develop or a tiny crack may form. The residual stress combined with the applied stress of bending initiates a larger crack. The next time it is bent, it may tear apart. Catastrophic failure is one outcome of the buildup of residual stress. ■ In some cases, residual stresses can enhance mechanical performance (e.g., "compressive" residual stresses can make a material less susceptible to cracking). However, many tensile residual stresses eventually lead to degraded mechanical performance, stress corrosion cracking, shortened lifetime, and even catastrophic failure.

One key to predicting failure in metal and ceramic objects is measurement of residual stresses.

The purpose of the center is to measure residual stresses in materials and components using X rays ... and neutrons.

David Schenk (a student from Tennessee Technological University), Steve Spooner, and Xun-Li Wang prepare for a residual stress experiment using neutron diffraction.

To prevent failure of an object, it helps to know when failure is likely to occur. Then you can pull the object out of service and treat, repair, or replace it before it fails. One key to predicting failure in metal and ceramic objects is measurement of residual stresses.

Such measurements are now being done at ORNL's Residual Stress User Center through nondestructive methods using neutrons and X rays. These measurements are important for various reasons. They help industry determine (1) which manufacturing processes minimize the generation of residual stresses, (2) whether an object can withstand service in demanding applications, and (3) whether heat treatment (annealing) of an object that contained residual stresses successfully eliminated or reduced them. These measurements help developers of computer models construct and improve their models so that they can more accurately predict when residual stresses of various sizes combined with externally applied stresses of various sizes would cause cracking and failure.

The Residual Stress User Center was established in ORNL's High Temperature Materials Laboratory (HTML) in 1993. (Other HTML user centers focus on machining and inspection, material analysis, mechanical characterization and analysis, physical properties, and X-ray diffraction.) Principal investigators for the Residual Stress User Center are Cam Hubbard, Xun-Li Wang, Kris Kozaczek, and Tom Watkins, all of the Metals and Ceramics Division, and Steve Spooner of the Solid State Division. The center staff interacts with researchers in the automobile, paper (see sidebar on p. 62), nuclear power, and aerospace industries as well as in universities. The purpose of the center is to measure residual stresses in materials and components using X rays provided by two custom-made instruments at HTML and neutrons provided by ORNL's High Flux Isotope Reactor (HFIR), which offers the highest neutron flux in the world for materials analysis. The User Program is sponsored by DOE, Office of Energy Efficiency and Renewable Energy, Office of Transportation Technologies.The HFIR is supported by DOE, Office of Energy Research, Office of Basic Energy Sciences.

To understand residual stress, consider arrays of atoms in parallel planes in a crystalline material. In the stress-free area of the material, the distance between the planes is constant and measurable. Assume that this material contains the two main types of residual stresses—compressive and tensile. These forces on the crystalline material cause lattice strains. Compressive stresses cause the distances between the planes to decrease, and tensile stresses cause the distances to increase in comparison with lattice spacings in a stress-free area.

A residual stress is calculated by measuring strains in three orthogonal directions—length, width, and height—

Cam Hubbard, Stan David, and Steve Spooner use neutrons at the High Flux Isotope Reactor to make the first map of residual stresses in a complex multipass weld.

in each of the material's "volume elements" (which are a few cubic millimeters in size). Strains in bulk materials can be measured by neutron scattering because neutrons penetrate several millimeters into a material. These neutrons scatter at different angles governed by the varying distances between the atomic planes. By relating scattering angles to interplanar distances at all locations, strains can be mapped, and residual stresses in bulk materials can be calculated.

Residual stresses are also classified according to their range. Microstresses are short-range stresses that vary from grain to grain in crystalline material. For example, because of thermal expansion, when a composite material such as zirconia in an alumina matrix cools from the forming temperature to room temperature, the zirconia particles may shrink more than the alumina matrix, creating a mismatch. These microstresses are compressive for one phase of the material while the other is placed under tension. Microstresses occur across distances no larger than a few millionths of a meter, or a micrometer. Such microstresses can lead to failure of parts during manufacture (cracking on cooling) as well as under static or dynamic loads.

Macrostresses, on the other hand, extend through a part over longer distances—typically a few thousandths of a meter, or millimeters. Macrostresses can be spatially resolved, or mapped. They are present in weldments and joining of dissimilar materials, and they arise from nonuniform cooling. These stresses are measured at the Neutron Residual Stress Facility at the HFIR. This facility consists of a neutron monochromator that provides a narrow beam of neutrons, all of the same wavelength. The neutrons diffracted from the specimen are recorded by a position-sensitive detector. The system is highly automated to provide measurements round the clock.

Stresses at or within a few micrometers of the surface of a material are better measured by studying the material using X rays. One new technique for profiling subsurface residual stress is called grazing incidence X-ray diffraction (GIXD). The X rays penetrate the material slightly and then backscatter out of the material, like a thrown pebble glancing off water in a pond. This technique is particularly useful for ground ceramics and photovoltaic coatings, and it is popular with users. The center's two X-ray diffraction instruments are equipped with high-precision goniometers that make possible highly automated data collection and analysis. The same instruments can also characterize texture or nonrandom orientation of crystallites, which occurs frequently when coating, forging, and hot pressing materials.

Bill Donlon of Ford Motor Company studies residual stresses in a disc brake rotor using neutrons at ORNL's Residual Stress User Center.

Neutron Studies

Ford Motor Company is looking for a way to improve disc brakes on its cars. Under severe use conditions, its disc brakes distort after overheating, leading to annoying vibrations during braking. Ford's goal is to reduce the cost of servicing brakes—to the company and the owner—over the lifetime of the vehicle. So Bill Donlon of Ford Research Laboratories and G. Vyletel of Ford Motor Company came to ORNL's Residual Stress User Center. They wanted to better understand the effect of residual stresses on disc brake rotors. These discs spin when the car is moving until the brakes are applied, hydraulically pressing pads with friction linings against the discs to slow or stop them—and the car. It is believed that when the disc brake rotors overheat, changes in residual stresses in the discs cause them to distort, leading to vibrations during braking. The

Neutron mapping studies at HFIR showed that strains in brake rotors can be reduced by heat treatment.

researchers wanted to test this hypothesis and to learn whether heat treatment of rotors would reduce distortions, making the rotors less likely to vibrate.

The Ford researchers brought to ORNL some standard rotors and some rotors that had been heat-treated to relieve stresses. Neutron-mapping studies at HFIR showed that standard rotors do have significant strains and that these can be reduced by heat treatment.

Residual stresses in joints between metals and ceramics are also being studied at the ORNL center to identify the process that makes the most reliable joints. In research involving DOE's Idaho National Engineering Laboratory (INEL), neutron measurements were made on nickel joined to alumina because of past disagreement between computer model predictions and experimental measurements of residual stresses. In the samples studied, joints made of nickel and alumina vary in their composition and structure from end to end. The mixtures of nickel and alumina changed in steps (with the alumina concentration being low near the nickel piece and high near the alumina piece). The residual stress measurements made by INEL's Barry Rabin at ORNL agreed with model predictions of residual stress sizes for different joint types. The information could lead to selection and modification of processes for making improved metal-to-ceramic joints.

Microstresses in silicon nitride were studied at the ORNL center by I. M. Peterson and T. Y. Tien, both at the University of Michigan. They were interested in the relationship between microstresses and fracture toughness, a material's resistance to cracking. The silicon nitride they studied has an aluminosilicate in its grain boundaries, microscopic areas between the crystalline silicon nitride grains. As the silicon nitride is heated with sintering aids containing magnesium, calcium, or barium oxide along with alumina and silicon dioxide, these grain boundary constituents become glasslike and serve as a glue that holds the ceramic particles together. It was found that microresidual stresses increased with the fraction of the volume that is occupied by the glassy-grain boundary material. The reason: while compressive stresses develop in the silicon nitride grains, tensile stresses develop in the grain boundary phase. It is believed that not only does glassy material bridge the silicon nitride grains but also that tensile stresses may assist crack deflection, increasing fracture toughness and minimizing the ceramic's susceptibility to cracking and failure.

X-Ray Studies

The GIXD capability at ORNL was developed in response to a user need. AlliedSignal came to the center for help in developing a quality assurance technique to check whether a vendor used the correct procedure in grinding silicon nitride parts for fuel metering in jet engines. If the incorrect grinding technique is used to finish this ceramic component, it can be damaged. Such damage could lead to unexpected failure or improper operation of the fuel system. So the ORNL center was used to measure the near-surface residual stresses to determine whether the ceramic was damage free. The researchers found that the conventional grinding technique produced stress gradients compressive at the surface and tensile within a few microns below the surface. Participants in the research included Rick Rateick, Philip Whalen, and Franz Reidinger from AlliedSignal. Subsequently, other users, including Ben Ballard and Paul Predecki from the University of Denver in Colorado and Warren Liao and Kun Li from Louisiana State University, have assisted with developing the technique and applying it to other materials such as photovoltaic coatings and other ground ceramic parts. Ceramics must be machined to exacting dimensions for use in engines. Development of proper grinding processes that do not adversely affect mechanical strength is being guided by ORNL's GIXD technique.

In the X-ray studies with Louisiana State University, ORNL researchers found that machined silicon nitride shows damage in the form of "steep stress gradients." They observed that the subsurface damage layer becomes deeper as the machining or grinding wheel speed increases.

In other X-ray studies at the Residual Stress User Center, GIXD provided the U.S. Navy with critical information about expensive machining. TRW and Vanderbilt University used residual stress data from the center to improve the design and performance of gas containers for air bags in automobiles. The University of Florida at Gainesville used the center to characterize diamond coatings.

X-Ray and Neutron Diffraction Studies

Using both X rays and neutrons for residual stress studies, scientists working at the ORNL center provided data on residual stresses in welds to help Lockheed Martin Manned Space Systems, Pennsylvania State University, and the University of Alabama refine knowledge of welds and weld repair procedures for a high-strength aluminum

Julia Bjerke of Caterpillar, Inc., uses X rays to study stresses in plasma-sprayed zirconia coatings.

George Rading of the University of Alabama and ORNL's Xun-Li Wang (left) use neutrons to study residual stresses around welds in aluminum for future space shuttle fuel tanks.

The center also has made contributions to the improvement of gears for automobiles.

alloy called Weldalite. Because it is a strong, lightweight alloy, Weldalite may be used to build a lighter external fuel tank for the U.S. space shuttle so that it can handle a heavier payload.

The center also has made contributions to the improvement of gears for automobiles. Studies at the center helped Penn State improve the quality of gears and aided DOE and industry in developing a computer model that predicts the ability of heat treatment to introduce beneficial residual stresses in gears being manufactured for automotive applications, including the first gear for General Motors' Saturn cars.

Summary and Outlook

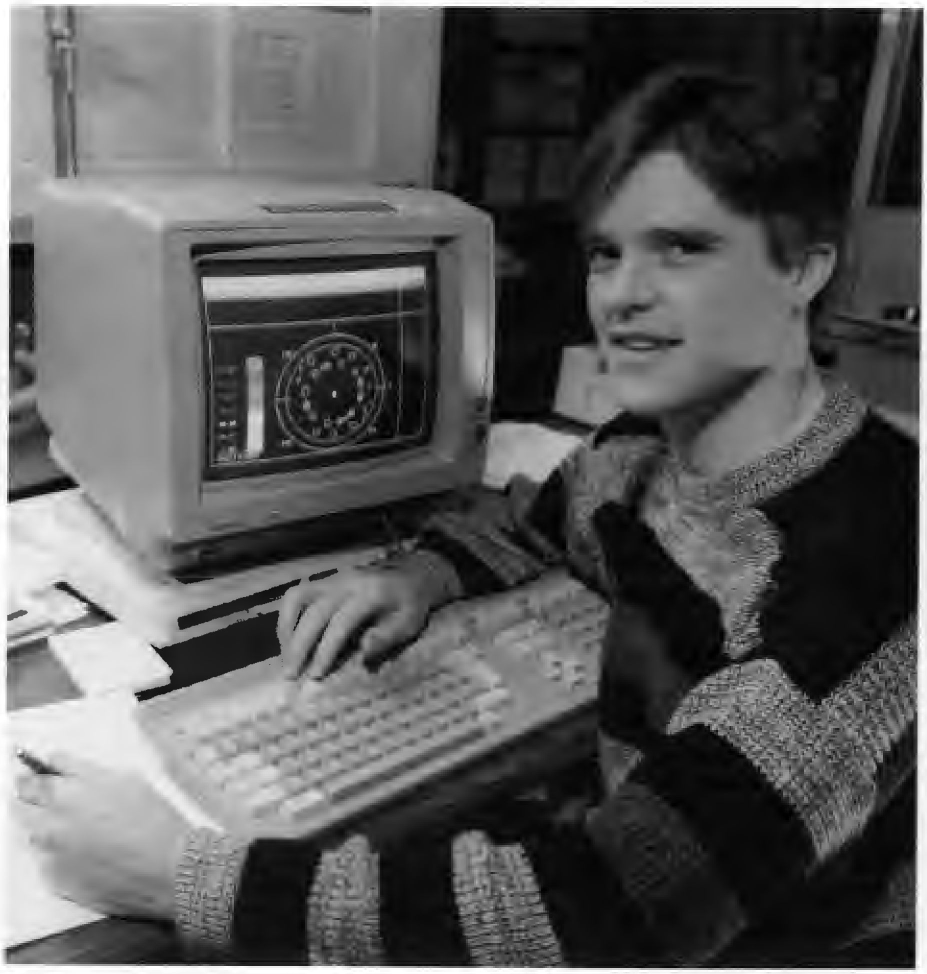
Since the Residual Stress User Center opened 3 years ago (the neutron faciliities have been available to users for 1 1/2 years), user activity has exceeded expectations. The center has been involved in more than 45 user research agreements as well as 3 DOE-sponsored programs and 4 proprietary projects for industry. To meet the surprising demand for the center's services, ORNL has developed office and instrument space at the HFIR; extended data collection and analysis methodologies; and established mechanisms for effective user support.

To speed neutron residual stress measurements, a seven-detector array was designed, assembled, tested, and installed in the fall of 1995. This detector array will permit ORNL to better characterize the strains in materials more completely and more rapidly. Plans have

It is believed that tensile stresses may assist crack deflection, increasing fracture toughness in silicon nitride.

been made for the design and construction of a dedicated neutron strain mapping instrument involving better neutron monochromators and improved beam delivery. This instrument will be automated, remotely monitored and controlled, and capable of complete data analysis. Our goal is a tenfold enhancement of existing capabilities. Advances in the X-ray facilities are also planned to serve user and DOE program needs.

In short, because design engineers need knowledge of residual stresses in materials to produce reliable, safe, and efficient designs of components, the need for residual stress measurements grows. ORNL is making every effort to meet the need and fill the information gaps. **ornl**



Andrew Hunt, a student at Georgia Institute of Technology, uses X-ray diffraction to assess the effectiveness of a novel thin film deposition technique. The screen image shows crystallite texture.

Anantha R. Sethuraman of Rodel, Inc., Newark, Delaware, uses X rays at ORNL to look for residual stresses in silicon wafers as part of a project to study the effects of polishing on stresses in metal interconnect structures.

How ORNL Helps the Paper Industry

Recovery boilers, however, have a problem: they can fail unexpectedly.

The recovery boiler is a critical, and certainly the most expensive, component of paper mills that use the Kraft process to produce pulp from wood chips. This most widely used pulping process enables the production of dark paper used for wrappings, envelopes, and grocery bags and, after bleaching, white paper used for printing or personal cleanliness.

Recovery boilers, however, have a problem: they can fail unexpectedly. Over the past 40 years in North America, about two boilers a year have exploded. Sometimes workers are injured or even killed, and the boiler usually is damaged. The downtime resulting from a boiler failure may cost a paper mill as much as $1 million a day. Continuing concern about the problem has led the paper industry to work with ORNL and other research institutions.

In the Kraft pulping process, wood chips are treated with a mixture of caustic soda and sodium sulfide in the digester vessel to separate wood fibers from lignin, the complex polymer that binds the fibers together. The concentrated waste stream from the digester, called black liquor, contains both lignin and spent pulping chemicals. From this black liquor, the recovery boiler separates chemicals for reuse in the pulping process and burns the lignin to produce steam. Steam is used to provide heat to various processing units, such as digesters and paper-making machines, and to produce electricity for use in other parts of the paper mill.

The steam is produced in the array of tubes that form the heat exchangers and walls of a recovery boiler. Because of the boiler's highly corrosive environment and high temperature and pressure, these tubes are subject to catastrophic failure. If a tube ruptures, high-pressure water can be released into the boiler. There on the floor, the water contacts molten chemicals. Because these chemicals are as hot as 800°C, the water instantly vaporizes upon contact, causing an explosion that can severely damage the recovery boiler.

The cause of the failure of bimetallic tubes in the lower portion of most recovery boilers is not known. However, failure mechanisms such as thermal fatigue, stress corrosion cracking, and corrosion fatigue have been proposed. Because of the nature of the stainless steel–clad carbon steel tubes (known as composite tubes in the boiler industry), high residual stresses can be generated when the tubes are heated. In all of the failure mechanisms suggested, residual stresses are an essential part of the environment required for each mechanism to work.

To help the paper industry unravel the mystery, a multidimensional project is being conducted that involves ORNL and U.S. and Canadian paper institutes in cooperation with boiler tube suppliers, boiler manufacturers, and most major paper companies. This program involves an industry-wide survey to define all that is known about tube failures, a thorough characterization of the environment to which the tubes are exposed, residual stress measurements to define the stress state of composite tubing, computer modeling to predict the stresses experienced by the tubes during boiler operation, and laboratory fatigue and corrosion tests in environments like those of recovery boilers. It is hoped that this work will lead to alternative materials or operating procedures to prevent tube cracking.

As part of the effort to unravel the mystery, Xun-Li Wang and Camden Hubbard of ORNL's Residual Stress User Center are working to identify stresses in boiler tubes that could lead to a tube failure.

"Cracks have been found in composite steam tubes after service," Hubbard says. "We think some cracks form from stress corrosion cracking brought on by residual stresses introduced during manufacture and made worse by thermal and fatigue effects and mechanical stresses from pipe bends and other constraints. Our early results show significant differences in residual stresses in boiler tubes from different manufacturers and with different clad coatings. We hope to identify the materials that hold up the best. We will provide data for computer models that simulate the elevated temperature operation and use of improved tube materials that may extend the service life of recovery boilers."

"The paper industry," Hubbard says, "hopes the research will lead to improved materials that will have two benefits for recovery boilers. One is enhanced safety by decreasing the chances of tube failure and boiler explosions. The other is increased efficiency by allowing increases in boiler operating temperature and pressure and by reducing downtime."

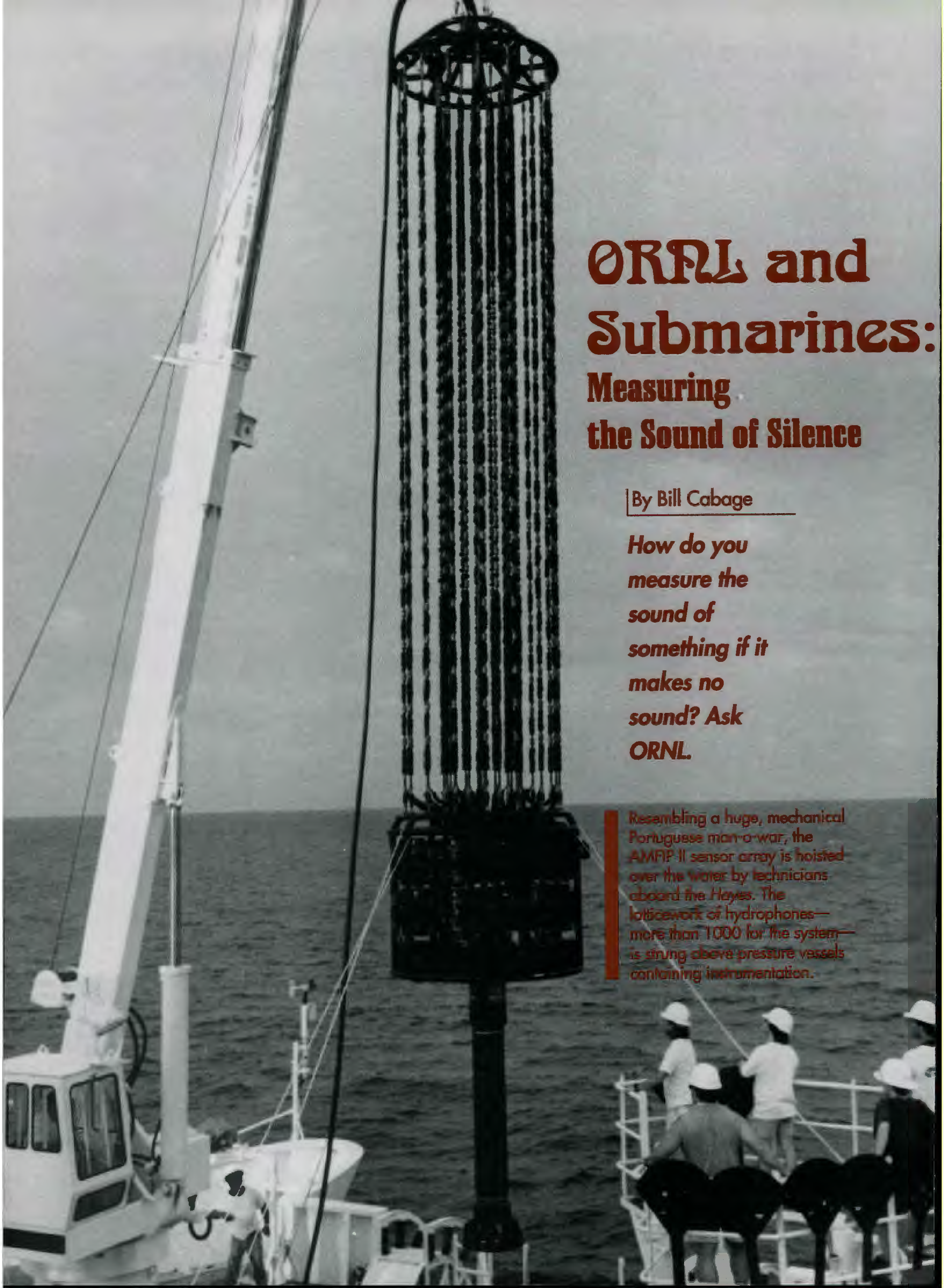
Neutron diffraction measurements are being made to characterize stresses inside straight tubes and in tube bends and welds. The measurements are being made at room temperature; in the future, they will be made at higher temperatures. Stresses on tube surfaces under fieldlike conditions are being measured using X-ray diffraction.

In addition, ORNL is using advanced computer modeling to simulate the operation of a recovery boiler and calculate internal stresses at high temperatures typical of normal and abnormal operation. The hope is that by modeling the materials, components, and stresses in a recovery boiler system, scientists will be able to better understand causes of failure and to predict time of failure under various conditions. The computer modelers will use data from ORNL's Residual Stress User Center, such as room-temperature residual stress measurements in steam tubes, to help make their model predictions more accurate.

The ORNL researchers are working with a team of researchers from a group of 11 pulp and paper companies (including Weyerhaeuser, Georgia-Pacific, International Paper, and Union Camp) and five major boiler suppliers, including Babcock & Wilcox and ABB Combustion Engineering. Besides ORNL, research sites for the project include the Institute of Paper Science and Technology in Atlanta and the Pulp and Paper Research Institute of Canada in Vancouver, British Columbia.

The work is sponsored by the Advanced Industrial Materials Program, Office of Industrial Technologies, Energy Efficiency and Renewable Energy, U.S. DOE. It is hoped the capabilities brought to bear on these problems will benefit the paper industry.

Our early results show significant differences in residual stresses in boiler tubes from different manufacturers and with different clad coatings.



ORNL and Submarines:

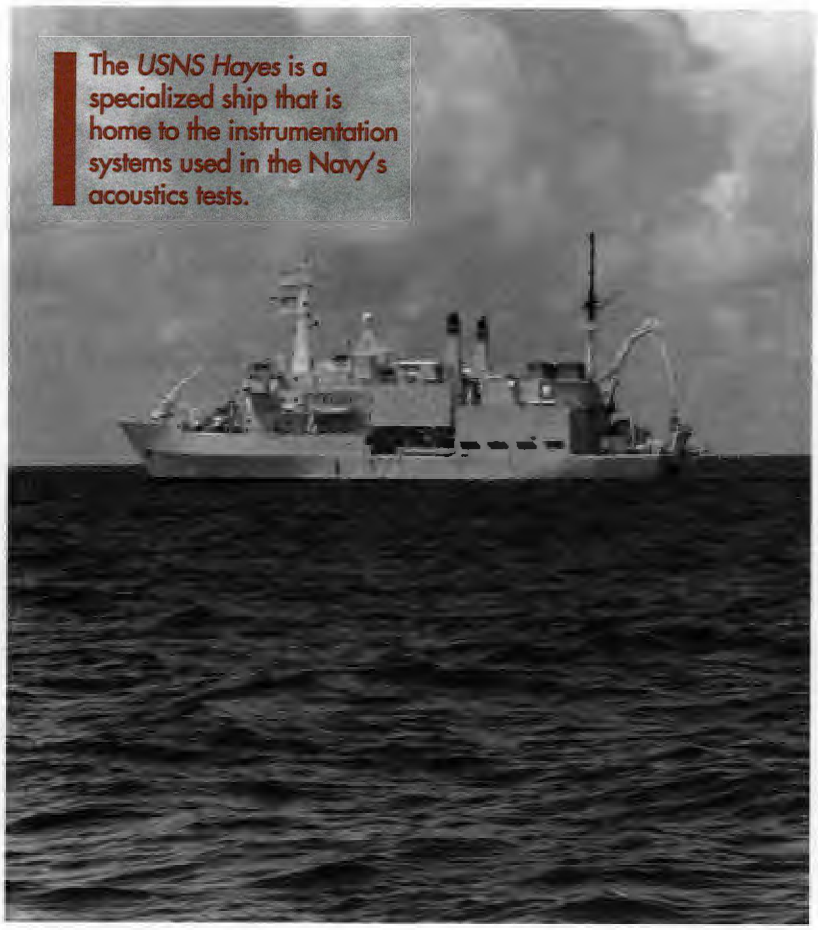
Measuring the Sound of Silence

By Bill Cabage

How do you measure the sound of something if it makes no sound? Ask ORNL.

Resembling a huge, mechanical Portuguese man-o-war, the AMFIP II sensor array is hoisted over the water by technicians aboard the *Hayes*. The latticework of hydrophones—more than 1000 for the system—is strung above pressure vessels containing instrumentation.

Silence is the hallmark of the United States Navy's nuclear submarines. Because they stay well out of sight below the surface of the water, enemies can detect them only by the sound they make. Consequently, they are designed to ply the seas as quietly as possible—the aquatic version of stealth technology. Many of those quiet technologies are closely guarded secrets.



The *USNS Hayes* is a specialized ship that is home to the instrumentation systems used in the Navy's acoustics tests.

This new technology can detect sounds below the ocean's background noise.

The Navy prefers to call its subs "quiet underwater weapons platforms." What little noise they do make must still be monitored in operational tests, both to improve designs and to ensure that the craft are operating to specifications. The testing requirements presented engineers with a challenge: how do you measure the sound of something if it makes almost no sound? Ask ORNL. The U.S. Navy has relied on ORNL's

Staying hidden is part of the submarine's job. Acoustics is one of the few ways these ships can be found.

Instrumentation and Controls (I&C) Division's expertise in electronics, real-time computer applications, and systems integration to develop state-of-the-art acoustic measurement systems.

ORNL has been working with the Navy on a special program for the past 6 years called AMFIP II—the second phase of the Acoustic Measurement Facilities Improvement Program. According to Randall Wetherington, who heads the program in the I&C Division, ORNL has devised ways to "measure the undetectable" for its sponsor, the Naval Surface Warfare Center's Carderock Division.

The system uses several arrays of hydrophone sensors—laceworks of underwater microphones suspended from buoys—to gather sound from the craft as it goes by. Computers process the sound signatures to extract the signal from background noise. "Waves and wind cause an ambient noise level in the ocean," Wetherington explained. "This new technology can detect noises below this ambient level. It's like a TV satellite dish in that the array, like the big dish, focuses the energy, which amplifies the sensor signals. As you add sensors, with their placement based on sophisticated math and geometry, you get more signal gain over a large bandwidth."

Much of the signal processing hardware and software for I&C Division's AMFIP II system is currently aboard the Navy's laboratory research ship the *USNS Hayes*, which is currently ported at Cape Canaveral, Florida. When test runs for submarines are scheduled, the *Hayes* sails to the test course set up in Exuma Sound, which lies in the middle of the Bahama Island chain. There the arrays, which have more than 1000 individual hydrophone sensors each, are placed to pick up sounds from the vessels as they pass through the course. Long umbilical cables connect the arrays to the rest of the system, which is located aboard the *Hayes*.

The radiated noise emanating from the Navy's submarines, called the acoustic signature, is normally low enough to be masked by the natural background noise of the ocean in a conventional hydrophone setup. The next generation of nuclear submarines—the *SSN 21 Seawolf*—operates below this natural background, requiring the world's most advanced underwater acoustic measuring system to ensure that its acoustic emissions remain below design limits and thus stay hidden beneath the vast ocean.

The initial problem, says Andy Andrews, deputy program manager in the I&C Division, is how to measure something that makes virtually no sound. "Staying hidden is part of the submarine's job," Andrews says. "Acoustics is one of the few ways these ships can be found. The craft in the *Trident* class can be the length of two football fields and not make any noise as they go by. Our systems help characterize the normal acoustic signature of the

As are many a sailor's, shipboard accommodations aboard the *Hayes* are spartan.

Our success in identifying new technologies produced significant cost savings for the Navy.

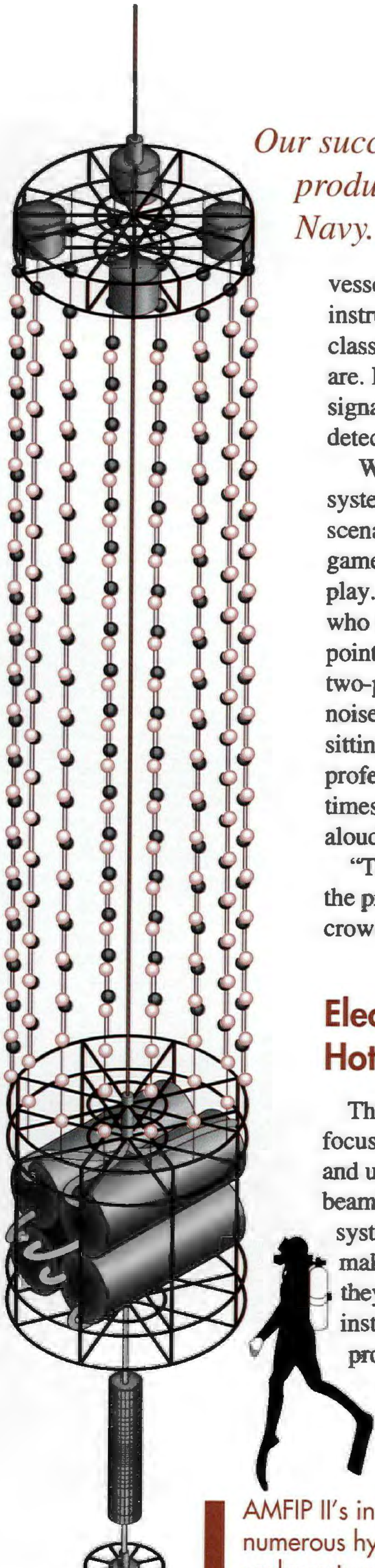
vessel as it runs through a course of instrumentation. Our system is not classified, although the data it generates are. If you know what a vessel's acoustic signature is, you could develop ways to detect it."

Wetherington likens the AMFIP II system's acoustic feats to a familiar scenario: "It's the Tennessee-Alabama game at Knoxville in the last minute of play. The score is 28-27, and Alabama, who has just scored to come within one point, is lined up to try for a go-ahead two-point conversion. Imagine the crowd noise from about 100,000 people. Now, sitting near the 50-yard line is an English professor with a heart condition who, in times of stress, calms himself by reciting aloud Edgar Allen Poe's *Annabelle Lee*.

"This acoustic technology could pick the professor's poem out of all of that crowd noise."

Electronics and Hot Rod Chips

The ORNL researchers' efforts have focused on three main areas—telemetry and underwater electronics; beamforming, or signal processing; and system integration, or, more simply, making it work. More generally, they've designed and built electronic instrumentation and developed a processing system that takes the data and generates information in a usable form.



AMFIP II's instrument arrays feature numerous hydrophones and sophisticated underwater electronics.

The telemetry system was a challenge to the I&C AMFIP II team because of the large number of signals from the sensor arrays that must be acquired, conditioned, and transmitted. These signals have a very wide bandwidth and must be transmitted over a long distance. The system required the identification and use of emerging technologies that arrived on the market at the same time that the design effort was initiated, making AMFIP II truly state of the art. The AMFIP II team had to clear technical hurdles presented by power distribution, heat dissipation, high-speed and high-resolution signal digitization, and very high-speed data multiplexing—combining information cascading in on multiple lines into a single line suitable for fiber-optic transmission.

"We used a 'hot rod' multiplexer chip developed by DARPA that combines information on 40 lines into a single line," Andrews said. "Our success in identifying new technologies produced significant cost savings for the Navy. For instance, we convert signals from the hydrophones to digital data almost immediately, which gives us very high-resolution signals, and then transmit the data by fiber-optic cable to the test ship. We identified a $20 digitization chip that will do tasks that used to cost $3000 per channel. We built three systems with more than 1000 channels each—one channel for each sensor."

Along with combing the marketplace for available electronics, the AMFIP II team also oversaw a large subcontract effort required by the construction of around 1300 multilayer printed circuit assemblies of 50 different designs, 22 equipment chassis, and countless cables and test fixtures. All of this, as well as automated test equipment to verify that they were all working properly as they were being made, had to be designed, *A major advantage of the system is that sensors can be monitored and diagnostics can be performed aboard ship.*

fabricated, and integrated into the final system.

When something breaks, as is apt to happen in a network of thousands of hydrophones, AMFIP II features a built-in diagnostic system that enables the technicians to quickly pinpoint the trouble, right down to the dead hydrophone or defective integrated circuit. A major advantage of the system is that sensors can be monitored and diagnostics can be performed aboard ship, a luxury much appreciated by technicians who would otherwise have to hoist arrays of a multitude of sensors and instrument cylinders aboard to troubleshoot. "It takes an incredible amount of computer power just to do the testing," Andrews says, but it's obviously worth it. The system also allows operators to monitor system degradation in the circuitry that is immersed in the salty, high-pressure environment.

Signal Processing: On the Beam

The beamforming, or signal processing, capabilities of AMFIP II produces the high-quality measurements and acoustic images of the submarines. The image beams are computed in real time for up to 35 frequency bands

Like a number of ORNL researchers involved in the AMFIP II project, Randall Wetherington (left) and Andy Andrews have made a number of trips to the Bahamas' Eleuthera Island, which lies near the Navy's test course in Exuma Sound.

simultaneously. The data from the hydrophones bobbing in Exuma Sound pours into the *Hayes* at a mind-boggling rate of 165 megabytes per second. I&C Division researchers Eva B. Freer and Bill Zuehzow have been instrumental in developing the algorithms and structure that bring all of the data into a usable configuration.

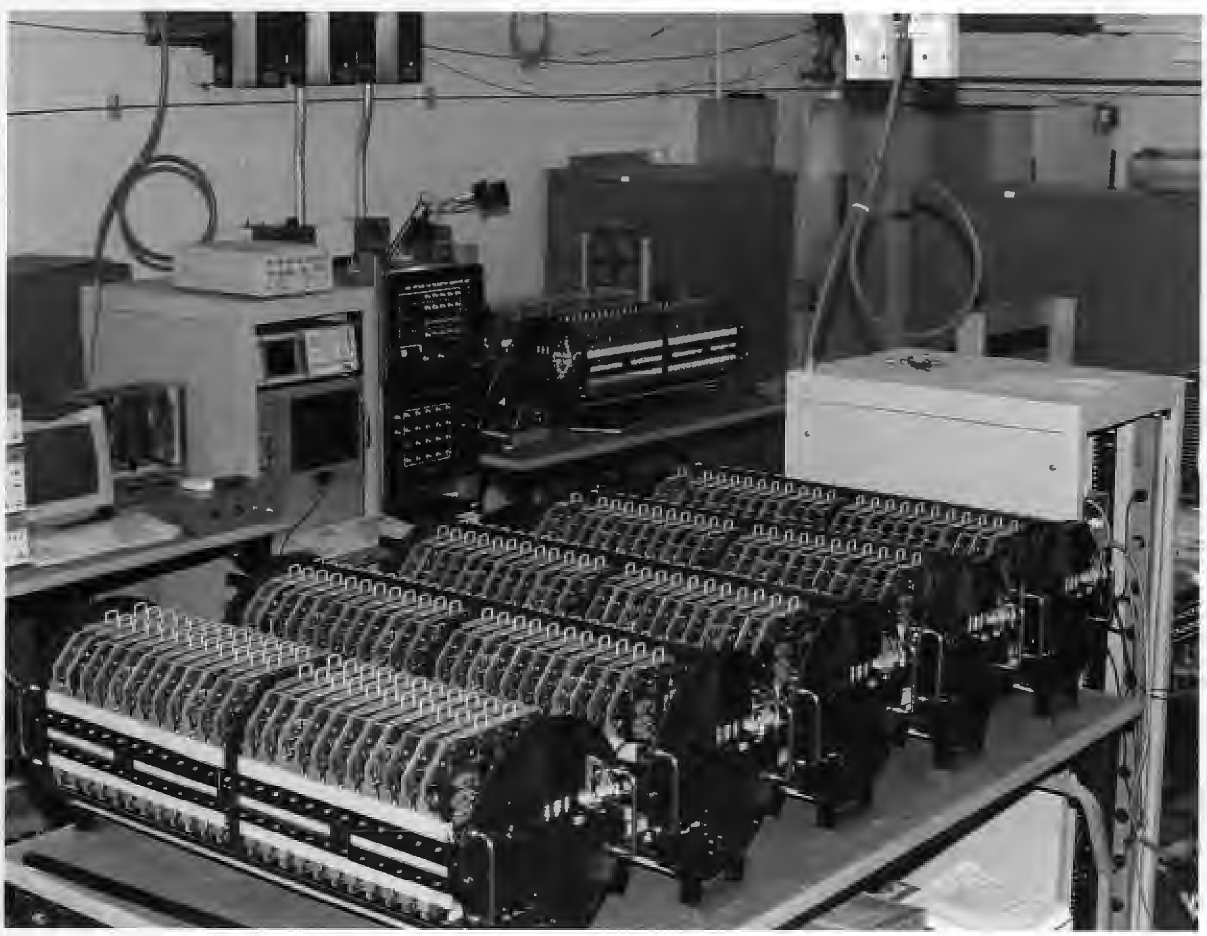
"To get a sense of how much information that is, a 3.5-in. floppy disk holds 1.4 megabytes," Freer says. "That's 115 full high-density floppy disks per second for each array!

"The custom electronic equipment aboard ship preconditions the data using more than 40 billion fixed-point instructions per second from embedded digital signal processing chips. This preconditioning is done even before the supercomputers process the data. The ability of this system to collect a multitude of signals and increase their gain with the computer algorithms enables the system to raise the submarines' image from the ocean's background noise."

As might be imagined, handling data from thousands of instruments takes a huge amount of computing power. Devising ways to handle and analyze the amount of sensor data coming in at this rate takes very specialized programming, and that is a specialty of I&C's Real-Time Systems Group. I&C Division was home to a 40-gigaflop supercomputer—for a time the biggest at the Laboratory—to perform the signal processing algorithms. The result of all of this data crunching is the image of a ship, or at least its sound image.

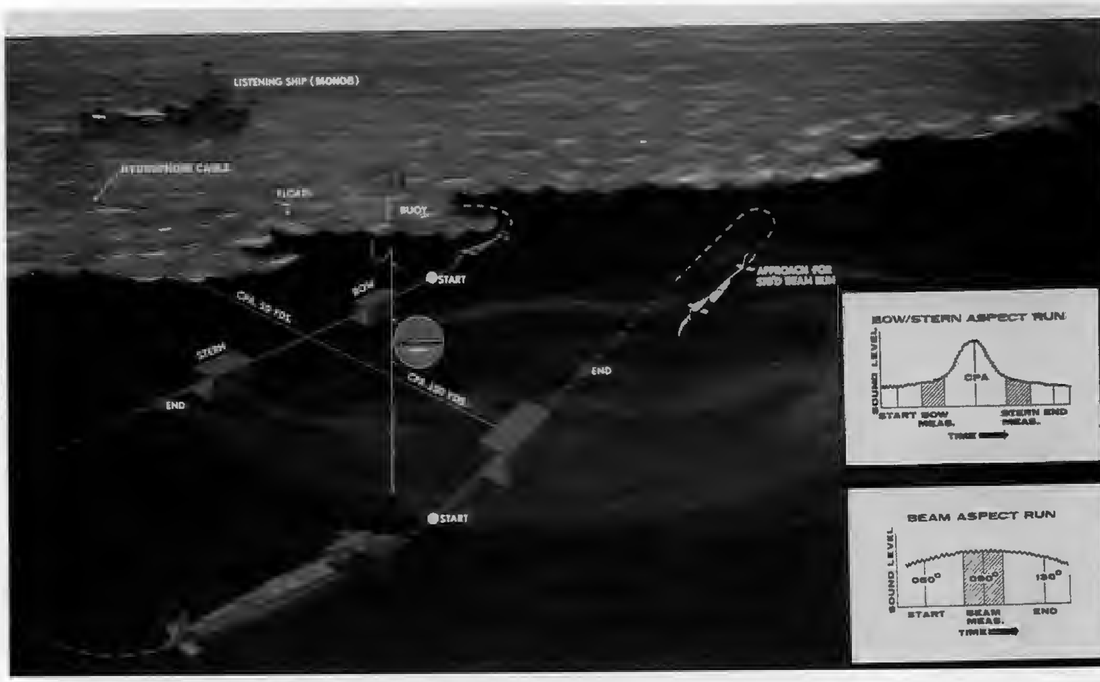
Building and Debugging

Because part of the system operates in seawater at considerable depth, it must be well built. The hydrophone arrays feature thick-hulled cylindrical instrument packages that are custom made by the Navy and pressurized with helium, which conducts heat away from the electronics. When something does malfunction, such



A sizable portion of the electronics for the AMFIP II system is housed in thick-hulled pressure vessels built to stay watertight in deep water. The system's printed circuit assemblies, which are contained in the vessels, number over a thousand.

The Navy's nuclear submarines run through a course to be monitored by the AMFIP II system's sensors. The staggering amount of data generated by the sensors is manipulated by the system's signal processors and powerful computers to produce the acoustic signature of a craft that makes almost no noise.



The Navy's test course is located in the Bahamas within a corner of the fabled and mysterious Bermuda Triangle. Researchers in the AMFIP II program like to point to this fact, although few express reservations about working after dark.

The acoustic signaling technology is also being considered for medical applications such as diagnosing a malfunctioning heart.

as a sensor going out, it can be detected and compensated for aboard the *Hayes*. Calibration of the system can also be done remotely.

"Close to half of our effort is for testing—proving that the system is working and debugging it when it doesn't," Wetherington said. "In all, the I&C Division and subcontractors have put about 30 years of conceptual development and prototyping, 20 work-years of software development and integration, and 10 years into electronics design, integration, and tests. We've also fabricated and performed quality assurance checks on 1300 multilayer printed-circuit assemblies."

The AMFIP II system consists of components and software from seven commercial suppliers, ORNL researchers, and three subcontractor teams. Putting together a product of the complexity of AMFIP II from these diverse sources required careful systems integration. "An important aspect of this project is the teamwork," Wetherington says. "ORNL had 147 staff members who worked on the effort. Our sponsor was very supportive and worked as a member of the team. We also had top-notch support from several subcontractors, including Planning Systems, Inc.; Cray Research, Inc.; Colonial Assembly and Design; and the University of Tennessee."

The I&C Division's AMFIP project began in 1986; the first acoustic processing system that ORNL developed was delivered in late 1989, and AMFIP II began soon after. The meticulous and ongoing attention to detail and project planning came to fruition again in October 1994 when ORNL successfully delivered and installed the first portion of the new AMFIP II measurement technology. The remaining components were installed in July 1995. The Navy sponsors have indicated that they intend to apply the technology to other tasks throughout the fleet. The acoustic signaling technology is also being considered for medical applications such as diagnosing a malfunctioning heart through its acoustic signature.

AMFIP II evolved from a project that played to the I&C Division's strengths in instrumentation, computing, and systems integration. The team of researchers also proved themselves in adapting to new projects and identifying when to go outside the Laboratory. They identified new technologies and coordinated a complex effort that involved six large organizations and a variety of engineering disciplines from electronics to high-speed computing. The astonishing stealth of the Navy's "quiet platforms," Wetherington said, made necessary the awesome amounts of data and the electronic and computing expertise and toil involved in harnessing that data. "All of that effort has been needed to lift one analog signal, a submarine's acoustic signature, up out of the ambient noise of the ocean."

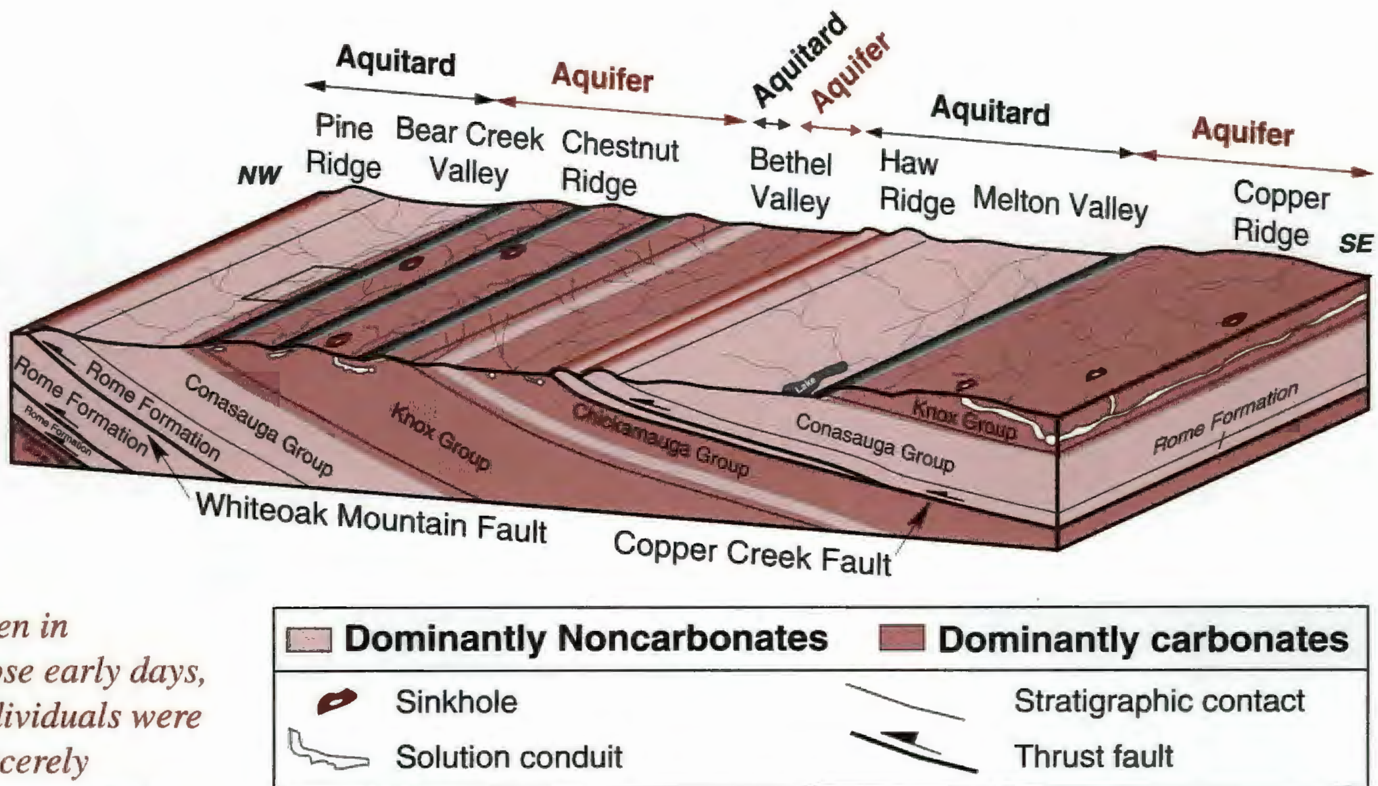
I&C Division researchers, who considered customer satisfaction as one of the most important goals of the program, count the Navy as a happy customer and the product that they have delivered as a giant step forward for their division. **ornl**

Earth Sciences and ORNL: A Long Partnership

By Stephen H. Stow

I was struck by the fascinating historical tale that unfolded.

In recent years the discipline of earth sciences at ORNL has grown in recognition. Asked to prepare an overview of the earth sciences in the Environmental Sciences Division (ESD) for the annual information meeting, I became interested in tracing their evolution before ESD was formed in 1972, as well as in exploring the truly interdisciplinary nature of the earth sciences since ESD was established: I was struck by the fascinating historical tale that unfolded. ■ What are the earth sciences? Some areas fall easily under this umbrella—geology, geochemistry, and hydrology (the science that treats the distribution, properties, and environmental behavior of water on the earth), for instance. Others, such as soil science, oceanography, and atmospheric systems, are less obvious. Many engineering disciplines, especially those dealing with chemistry, soils, and groundwater, can be legitimately included. The line of demarcation between areas of "earth science" and "life science" is poorly defined, a situation that seems to encourage interdisciplinary work, as we shall see.



Even in those early days, individuals were sincerely concerned about proper disposal of liquid nuclear waste.

Rock strata dip steeply into the ground of the Oak Ridge Reservation as shown in this diagram. Many of them, especially those of the Knox Group, are aquifers that transmit water rapidly, often through sinkholes and caverns. Others are aquitards in which water moves slowly, often in fractures.

Two factors basically underlie the earth sciences in ESD. These factors are waste disposal and biogeochemical cycling. The issues that are addressed by the earth sciences are, first, understanding the physical and chemical parameters influencing the movement and fate of energy by-products in the environment, and second, development and application of methods for controlling and monitoring that movement. With these thoughts in mind, I became interested in determining when the principles of earth sciences first surfaced here at ORNL and began a historical journey. (We fully recognize a parallel and excellent effort in geochemistry under Dave Wesolowski in the Chemical and Analytical Sciences Division that falls largely outside this discussion of history but that is covered in the following article.)

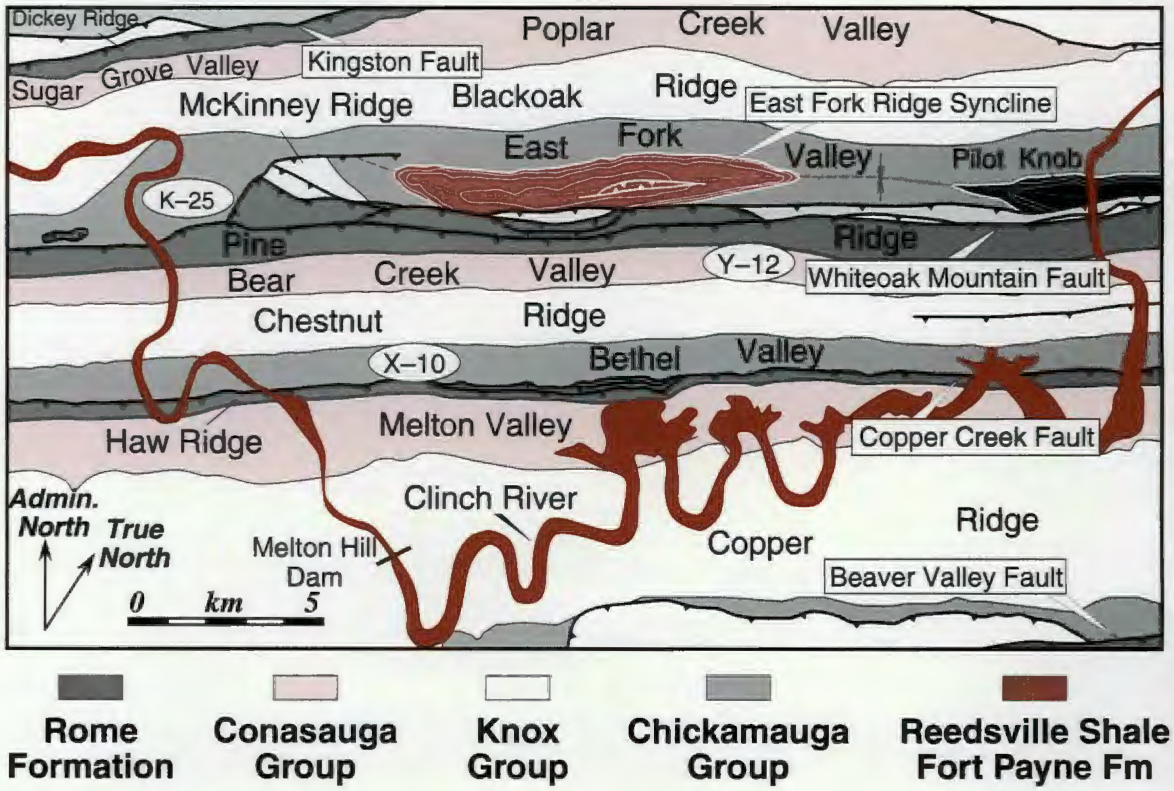
Three messages emerge from the story of the earth sciences in ESD: (1) they have been important to the operation of ORNL since the earliest days; (2) even in those early days, there were individuals sincerely concerned about proper disposal of liquid nuclear waste; and (3) the more things change, the more they seem to stay the same.

Early Years

In January 1944, ORNL's first solid waste storage area (SWSA) for low-level radioactive waste was established in Bethel Valley close to the laboratories. The second and third SWSAs were also sited there. Reviews of the history of waste disposal by Browder, Coobs and Gissel, and Webster all confirm that these facilities were sited largely for the convenience of employees at the labs rather than on the basis of principles of hydrology and soil chemistry. However, SWSA 1 was abandoned when water was observed in a disposal trench, suggesting a concern that water could carry hazardous materials into the human environment.

In reviewing Browder's 1949 article on liquid waste disposal here, I was struck by his phrase "it has long been known . . . waste constitutes a health hazard" and "necessity for . . . removing poisons from . . . wastes has been

The Oak Ridge Reservation is characterized by a series of linear outcrop patterns of sedimentary rocks. Thrust faults are common, as shown by the lines with triangular symbols. The geology of the reservation is the most complex of any DOE site.



Dilute and Disperse

In 1943, the original waste management concept was to hold all liquid radioactive waste in underground tanks for the single year that the Laboratory was expected to operate. However, the scope of the Laboratory expanded and the treatment process for separation of plutonium from the Graphite Reactor changed; it soon became evident that there was not enough storage capacity. The waste was then treated to precipitate essentially all the transuranic elements and many fission products, stored in settling ponds to allow precipitation and decay of short-lived isotopes, diluted with clean process water, and then discharged to White Oak Creek and Lake. In 1943, White Oak Dam was built across the creek to create the lake for this purpose. In regulated amounts, the waters from the lake were then discharged to the Clinch River for further dilution.

apparent for several years." Curiosity asks what were the attitudes toward "proper" disposal "several years" ago (see sidebar "Dilute and Disperse" at left). Laboratory Records helped provide interesting documents. For instance, a February 1946 memo from William H. Ray to Karl Z. Morgan, director of the Health Physics Division, describes the "discharge of wastes of abnormal activity for five days." It states, "That the protection of the drinking water systems of the Tennessee and Mississippi river valleys depends upon the correct handling of our liquid wastes cannot be overemphasized for those responsible for their protection. The taking of chances is unwarranted." Powerful words!

A 1944 letter from Martin Whitaker, then Lab director, addresses soil percolation tests and hydraulic gradients—measurements made to help ensure immobilization of the wastes from the settling basin. Earlier that spring, the hydrologic transport of contaminants in White Oak Creek had been a major issue of concern. Even before wastes were released to the creek system (March 1944), Morgan ran background analyses in White Oak Lake. Releases to White Oak Creek, White Oak Lake, and the Clinch River were carefully calculated and guided by medical knowledge of the time, documented in numerous historical memos. Space does not allow an expansion of this theme here, but the message that conscious attempts were made to control the releases of nuclides to the environment to prevent harm to human health is an important one that deserves more attention.

Another early earth science facet surfaces in a 1944 report on contaminated sediments in White Oak Creek. It was

The contorted and complex patterns of the sedimentary strata are shown here. Fractures in the rock made it difficult to contain liquid wastes disposed of in these pits.

This photograph shows the locations of the early disposal operations at ORNL and the drained lake bed of White Oak Lake. The "solid waste burial ground" in the upper left is Solid Waste Storage Area 4 (SWSA 4).

In 1948, the first real geologic mapping of the Oak Ridge Reservation was started.

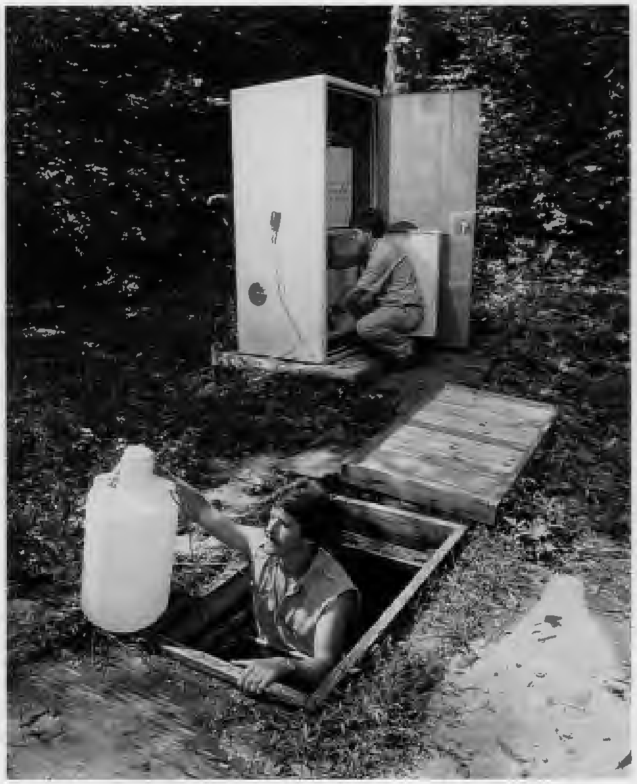
hypothesized that fission products were transported in colloidal form; many of us have thought that such a transport process was a revelation of recent decades—indeed it was not. It is also interesting to note that the ORNL Medical Department provided guidance in July 1944 to the Hanford facility in Washington on whether soil conditions there would allow safe disposal of radioactive waste in the ground. At the time, Hanford reactors were being readied to produce plutonium for use in the atomic bomb that ended World War II.

In 1948, the first survey of radionuclides in Watts Bar Reservoir was undertaken, representing a precursor to the Clinch River studies of later decades. Also, the first real geologic mapping of the Oak Ridge Reservation was started, but it would not be until 1962 that the first geologic map was published. I found it interesting that Laboratory management showed concern about liquid wastes, but not solid wastes, and paid attention to surface waters, not groundwater. Things would, however, change in a year or two.

Increased Awareness in the 1950s

In the early 1950s, 50 monitoring wells were constructed around the Bethel Valley SWSAs, and Paris Stockdale, head of the Geology Department at the University of Tennessee at Knoxville, recommended that the SWSAs be relocated to Melton Valley. He argued that Melton Valley would isolate nuclear waste better because of its shale-rich strata that take up and hold (sorb) radionuclides. He stated that the carbonates in Bethel Valley are prone to solution development—that is, they can be dissolved by infiltrating water, which could carry radionuclides away from the disposal site. So SWSA 4 was sited on shale just inside Melton Valley. However, it turned out to be too close to the floodplain of White Oak Creek. Ever since, ORNL has experienced problems with high releases of certain radionuclides into surface waters.

Also in early 1950s, changes were made in the way liquid wastes were handled. The pits—and later trenches—were used for disposal of some one million curies of radionuclides through the mid-1960s. Again, the sorption capacity of the Conasauga shales formed the basis for seepage systems that served as a giant ion exchange column, retaining most of the radionuclides and preventing their migration. Pits 4 and 5 were built to cross numerous bedding planes to maximize seepage, but the frustrations of rapid flow through fractures in the shale, when sorption did not occur, plagued the operation. Pump tests and geophysical well logging were used in the 1950s to help characterize the geology and hydrology of the pit and trench area. Evolving from this work and that at the SWSAs were pioneering experimental investigations in the late 1950s on the geochemistry of radionuclide sorption on mineral surfaces. Also, the first ideas of using hydrofracture for underground disposal of radioactive liquids were developed toward the end of the 1950s; this process would be used for several decades.



The movement of groundwater and its contaminants is studied at ORNL's unique subsurface facilities where researchers monitor groundwater flow at the lower end of Walker Branch Watershed. Phil Jardine works in the foreground; David O'Dell, back.

As a result of the passage of the 1954 Atomic Energy Act, which allowed commercial production of nuclear power, high-level wastes (HLW) became an issue also. Ed Struxness, a pioneer in ESD, and Morgan experimented with self-sintering, a process that is analogous to today's in situ vitrification (see sidebar "Self-Sintering and In Situ Vitrification" at left). Struxness and

Self-Sintering and In Situ Vitrification

Self-sintering, which was patented in 1959, was a process developed by Ed Struxness and K. Z. Morgan to isolate and immobilize nuclear waste. The goal was to convert the waste to a glass that was resistant to leaching by water. The concept was to let the energy released by the radioactive decay of the waste heat the waste enough to drive off the water and eventually produce a solid, sintered glass product. A mixture of liquid waste, Conasauga shale, limestone, and soda ash were the reactants. Experiments using artificial heat were conducted in the laboratory and in the field across from Pit 1. This technology was not advanced partly because of concern about whether radioactive gas emissions from the heated waste could be controlled.

Today, four decades later, we are using artificial heat to melt the formerly liquid waste disposed of in Pit 1 to produce a leach-resistant glass waste form in the ground. This technique, called in situ vitrification (ISV), was developed at DOE's Pacific Northwest Laboratory. The reactants are the waste, Conasauga shale, and limestone. One of the greatest concerns has been whether emission of cesium-137 in gaseous form during the melt can be controlled. A method managing these emissions has been developed and will be used during an ISV test in 1996 at ORNL.

Lee Cooper measures abundances of stable isotopes of oxygen, carbon, and nitrogen to help understand the mechanisms and rates of movement of materials in the environment.

The drained lake represented an opportunity for ... scientists to study radionuclide sorption on clays and ... radionuclide uptake by biota.

others attended a benchmark conference in 1955 at Princeton University that addressed the issue of land disposal of HLW from reactors for the first time; the ramifications of this conference and impacts on ORNL would be felt for literally over three decades (see sidebar "ORNL and High-Level Waste" on p. 78).

In 1955, White Oak Lake was drained for many reasons, and it remained that way into the 1960s. The drained lake represented an opportunity for earth scientists to study radionuclide sorption on clays and to work closely with ecologists in the study of radionuclide uptake by biota.

Finally, at the end of the 1950s, the Clinch River Project was initiated to understand more about the behavior of contaminants in surface waters and their distribution and ecological impact downstream from the Oak Ridge Reservation. In 1995, we are still involved with this project as part of a major environmental restoration program, and we draw heavily from the early research that was directed by Struxness and others.

ORNL and High-Level Waste

Based largely on its leadership in innovative treatment of high-level radioactive waste and its participation in the 1955 Princeton Conference, ORNL was named the lead organization for identifying a bedded salt deposit for siting a repository for permanent disposal of HLW from commercial nuclear power plants and other facilities. In 1958, a salt deposit near Lyons, Kansas, attracted interest. By the early 1960s, ORNL staff conducted experiments to simulate actual disposal of waste as Project Salt Vault was born. During the middle of the decade, canned reactor fuel assemblies were used for extended experiments, resulting in conceptual repository design in 1970, particularly by staff from the Chemical Technology and Engineering divisions. Progress was rapidly being made toward an actual HLW repository, but in 1972, things came apart as the state of Kansas adopted a resistant position. The government is now encountering resistance to the latest potential repository site of its choice—Yucca Mountain, Nevada.

Later in the 1970s, Oak Ridge was named as the leader for the Office of Waste Isolation (OWI), which was charged with examining a variety of rock types nationwide in search for viable candidates for a repository; OWI came to Oak Ridge largely because of ORNL's demonstrated leadership with Project Salt Vault. ORNL staff in many divisions provided technical and socioeconomic support for this effort into the early 1980s, even after OWI was moved to the Battelle facility in Columbus, Ohio. ESD became involved in the "Crystalline Rock Program" for the southern Appalachian Mountains and then participated with the Chemical Technology Division on a technical (geological, thermal, economic, etc.) assessment of various sedimentary rock types for HLW disposal from the early 1980s until 1988, when this activity was terminated. In addition, ESD provided earth science support to the Nuclear Regulatory Commission for repository design during the 1980s.

Dealing with water in direct contact with radioactive wastes in disposal trenches (like the trench shown here) is one of many environmental restoration challenges facing DOE site managers today.

Uncertainty in the 1960s

Many activities from previous years continued throughout the 1960s. Liquid waste disposal at the pits and trenches was finally stopped in 1965 when hydrofracture was eventually implemented. This disposal process consisted of mixing the liquid with cement and other additives and injecting it under pressure through a well into the same shale unit underlying SWSA 4. However, because of the dipping strata, the injection was 1000 feet deep. This technique was used for liquid disposal until the early 1980s. To prove the feasibility of hydrofracture and show that the subsurface fractures would remain at depth (and therefore the wastes in cement would not rise to shallow depths or come to the surface) considerable geologic work was conducted by Wally deLaguna, who had come from the U.S. Geological Survey to ORNL in the mid-1950s. However, little concern was shown about contamination of groundwater by injected wastes.

Project Salt Vault, the proposed plan to dispose of HLW in salt deposits near Lyons, Kansas, was well under way (see sidebar "ORNL and High-Level Waste" at left). Geologic and hydrologic studies led to the siting of a new burial ground, SWSA 5, at a better location than SWSA 4. In spite of ORNL's having learned a lot about environmental protection over the previous 10 years, there

During this decade ESD staff became heavily involved in chemical studies of non-nuclear solid waste.

was still a lack of attention given to monitoring groundwater around the disposal sites, primarily because the Atomic Energy Commission did not recognize the importance of this transport medium and did not support such studies.

In 1967, the Walker Branch Watershed project got under way. The primary emphasis of this project was on ecological aspects of the watershed, including the biogeochemical cycle, the chemical interactions between biological materials and chemicals in the atmosphere, soil, groundwater, and surface waters. But there emerged a fairly heavy emphasis on earth science studies associated with soil chemistry and hydrology. Indeed, this project represented one of the best integrated studies drawing on the life and earth sciences, and it persists today in investigations of subsurface transport phenomena.

Earlier, as a graduate student in 1963, I wrote to deLaguna asking about summer employment. I saved his reply, which offers an insightful view of those times—one that translates to the present. He wrote one sentence: "Dear Mr. Stow, Our program is so uncertain I have little idea where I will be or what I will be doing next summer." The more things change, the more they seem to stay the same.

Diversity in the 1970s

Many new activities were started during this decade, and others persisted from the previous one. One of the most significant events was the cancellation of Project Salt Vault after decades of work because of resistance by the state of Kansas (see sidebar on "ORNL and High-Level Waste" on p. 78). ESD was formed as a division in 1972 and, in 1975, an Earth Sciences Section was

For decades, ORNL researchers have monitored the nature and extent of contaminants that have entered the river system to the south. Here, staff members Clell Ford (right) and university students Pam Krahl (center) and Suzanna Schorn prepare to take sediment samples from the river bottom.

The original hydrofracture facility is shown in the center of the picture, with the new facility in the foreground. SWSA 4 is in the upper left corner and SWSA 5 lies behind the old hydrofracture site. These burial grounds contain low-level radioactive wastes.

established. During the early 1970s, the National Science Foundation started the Ecological Analysis of Trace Contaminants Program. In reviewing this program's activities at ORNL, I noticed that the type of research performed involved low-temperature aqueous geochemistry with heavy emphasis on applying principles of earth sciences. Some eight ORNL divisions were involved in development and application of instruments for measuring concentrations of elements and isotopes in natural systems, sediment transport of heavy metals, behavior of toxic metals in soil and stream systems, computer simulation of sediment loading in reservoirs, and transport modeling. It was a really heavy "earth science" effort in close coordination with ecology, a point that emphasizes the highly interdisciplinary nature of our science.

During this period, increased emphasis was placed on understanding the behavior of carbon in the environment. The global carbon program was initiated and, although relatively few earth scientists were actively involved, again the principles of geochemical cycling and atmospheric dynamics brought a very

Ed Struxness

Ed Struxness had a strong influence on ORNL activities in the earth and life sciences. He was instrumental in organizing and implementing the early Clinch River study. He provided insights on the need to apply principles of geology, geochemistry, and hydrology to properly dispose of HLW, as well as low-level waste in the ORNL SWSAs. His guidance was essential to building a foundation to ensure environmentally safe disposal. His innovative development of self-sintering technology for high-level waste disposal was one major reason for his involvement in the Princeton Conference in 1955, which led directly to ORNL's decades-long leadership in repository siting. Along with Wally deLaguna, Struxness helped develop hydrofracture, which was a good disposal methodology at the time for the fission product waste it was designed to handle. Finally, Struxness had the foresight to hire Stan Auerbach, who became the first ESD director and carried on the effort to develop the earth sciences at ORNL.

A group of scientists in ESD became internationally known for their interdisciplinary approach to understanding the global carbon cycle.

interdisciplinary flavor to the effort. Over the years this program spawned a small group of scientists in ESD who became internationally known for their interdisciplinary approach to understanding the global carbon cycle. In addition, this program was a basis for establishment of the Carbon Dioxide Information and Analysis Center, which handles data and information analysis on carbon dioxide and its impact on global change.

Although considerable attention has been given in recent years to geologic and hydrologic aspects of ORNL's SWSAs, it was not until the early-to-mid-1970s that real effort was directed toward hiring new earth sciences staff and toward a more focused program for the burial grounds. Studies were initiated at the SWSAs to quantify and characterize contaminated soil and groundwater so that a better understanding of the mechanisms for radionuclide migration could guide selection of the most effective remedial actions. The latter part of the decade saw a major effort evolve in studies to identify and measure concentrations of contaminants in soil and groundwater at the SWSAs, leading to application of new in situ engineered barriers designed to inhibit radionuclide movement. Sophisticated groundwater modeling supported this work and monitoring of streams in Oak Ridge Reservation watersheds was used to understand hydrologic balances and the effects of the remediation.

Finally, during this decade ESD staff became heavily involved in chemical studies of non-nuclear solid waste and other materials. Diverse projects directed at the characterization of leachates from coal and coal ash, organic-rich shale, industrial waste, and sanitary landfills emerged so that the toxicity of the leachates and their impact on groundwaters could be assessed.

During the last part of the decade, Ed Struxness retired. Although a biologist by professional training, no other single person did more to shape the development of the earth sciences at ESD (see sidebar on Ed Struxness on p. 80). His vision, organizational skills, and leadership were truly unique in building the diverse programs.

To locate historical disposal sites or to identify karst cavities through which groundwater flows, ORNL scientists have developed highly sensitive geophysical methods for imaging objects below the surface. Here, Bob Kennard performs a subsurface study.

Remedial Actions and the 1980s

By now ESD had a reasonably large number of earth scientists on staff, and the attention given to proper management of ORNL's burial grounds had grown considerably with more field, hydrologic, and engineering projects and state-of-the-art computer modeling of contaminant transport phenomena. In addition, the National Low-Level Radioactive Waste Program was managed for DOE out of ESD, and we began to provide hydrogeologic support to the Oak Ridge Y-12 Plant, an initiative that would grow there and elsewhere. In recognition of the need for a more basic understanding of the physics and chemistry of the behavior of contaminants in the subsurface, DOE started the Subsurface Science Program, and ESD was heavily involved. Unique and highly sophisticated subsurface

ORNL's Mercury Expertise

Although ESD has been involved in the study of many contaminants, the one contaminant most associated with the division is mercury. Beginning in 1972, the National Science Foundation's Ecological Analysis of Trace Contaminants Program supported fundamental studies of the behavior of mercury in the Holston River, and ESD staff published a benchmark article on mercury emissions from industrial wastes in *Nature* in 1977, the same year that staff were asked to advise the Spanish government on the toxicity of mercury associated with the new Almadén mine.

ESD was intimately involved with the revelation in the early 1980s that large amounts of mercury had been released to the environment at the Oak Ridge Y-12 Plant, and it was ESD staff who were marshalled into a role of providing technical guidance to the Y-12 Plant and to DOE on the extent of the mercury contamination, ways to control and monitor it, and finally ways to remediate it. The fundamental work on micrometeorology of mercury from fossil fuel combustion and its global distribution is heavily rooted in the efforts of a few ESD staff, and the 1995 Environmental Protection Agency report to Congress on atmospheric releases of mercury drew heavily on information generated by ESD. The international recognition of Steven Lindberg and Ralph Turner for their pioneering research on this elusive metal is well deserved. (For a detailed description of recent ESD achievements in mercury analysis and removal, see the stories beginning on p. 111 in "Technical Highlights.")

For the first time in over 40 years, there are almost no high-level waste activities at ORNL.

facilities were constructed in Melton Valley and Bethel Valley for soil, hydrogeochemical, and modeling studies.

Perhaps one of the most widely publicized incidents of the decade involved the release of information on mercury losses from the Y-12 Plant over the years. This event catalyzed DOE's development of a more formal program of environmental cleanup at its sites across the nation, and ESD staff drew on their decades-long experience with mercury to help out. ESD leadership continues in its studies of the environmental behavior of mercury today and its developments of techniques to measure mercury concentrations and clean up waste containing mercury. (see sidebar "ORNL's Mercury Expertise" at left).

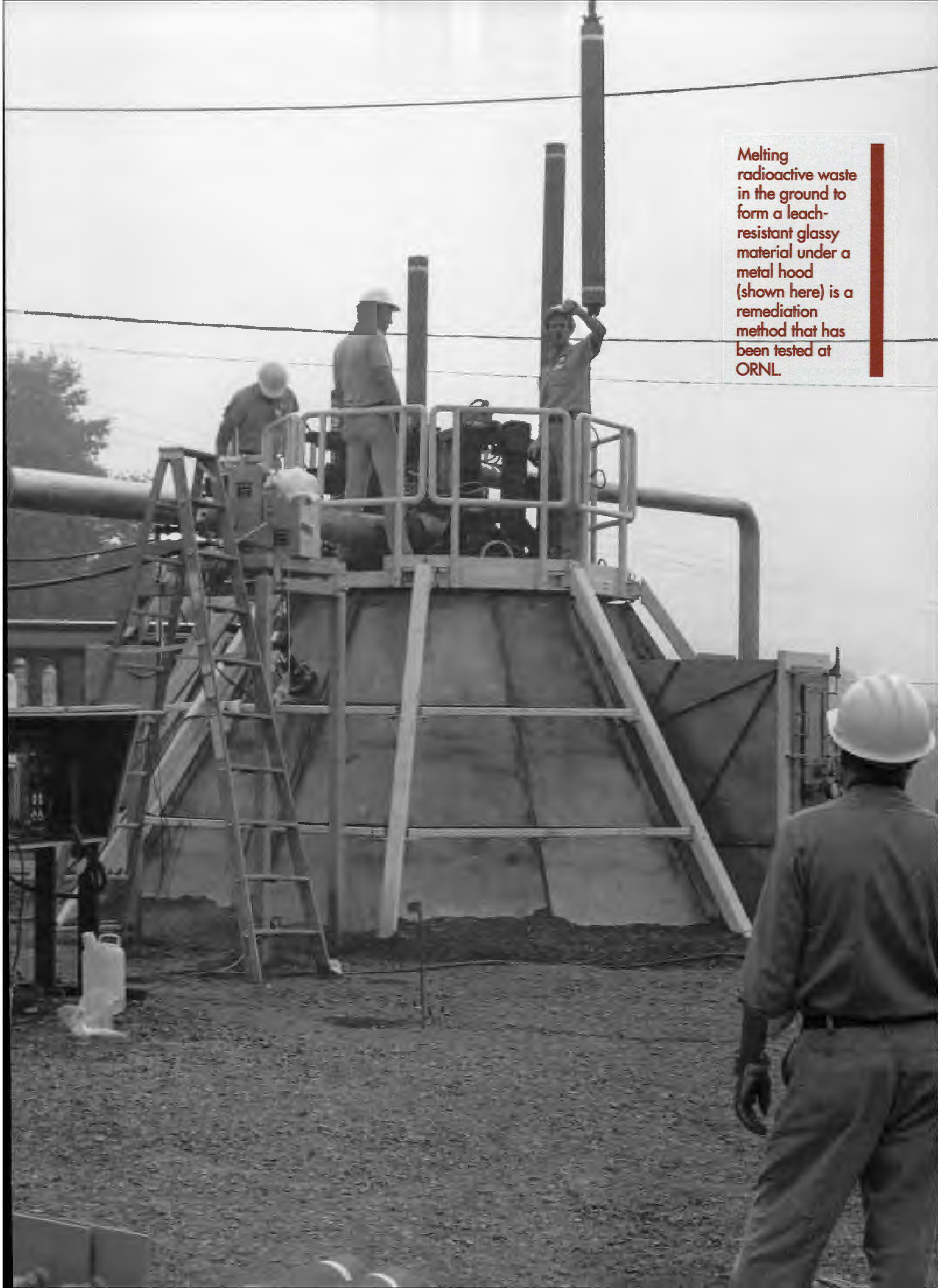
Other new initiatives got under way. The study of wet and dry deposition of gases and particulate matter, including acidic matter, onto forest systems led to development and application of top-quality measurement systems and innovative sampling strategies. The Integrated Forest Study, dealing with the biogeochemical cycling of nutrients in soils and forest systems, was a large work-for-others project in ESD. Studies of the transport and fate of trace metals, organics, and nuclides (natural and anthropogenic) in river-estuarine and coastal environments and isotope studies of snow melt and marine arctic systems were also significant activities. Research on non-nuclear solid waste continued well into the decade, and ESD supported the Health Sciences Research Division in opening an office in Grand Junction, Colorado, where field-oriented restoration work continues today.

A new hydrofracture operation was started, and another 750,000 curies of activity were injected between shale layers. However, this time problems were experienced in the well and injection procedures; the demise of the technology followed swiftly, leaving a legacy that, depending on the outcome of environmental restoration investigations, could be frightfully expensive to rectify.

The 1990s

The decade started with the loss of two highly valued staff members. Bill Boegly, Jr., an engineer who had been active in Project Salt Vault, self-sintering, remedial actions, and construction of the main ESD building, died after a bout with cancer. Ernie Bondietti, internationally known for his work on actinide geochemistry and soil systems, died as the result of an auto accident following a scientific conference. Their losses were felt throughout the division.

For the first time in over 40 years, there are almost no HLW activities at ORNL (see sidebar "ORNL and High-Level Waste" on p. 78). ESD work is dominated by innovative initiatives directed toward environmental restoration on the Oak Ridge Reservation, as well as at the Paducah and Portsmouth uranium enrichment plants, and elsewhere. In situ treatment technologies designed either to destroy or to immobilize contaminants or to prevent their interactions with



Melting radioactive waste in the ground to form a leach-resistant glassy material under a metal hood (shown here) is a remediation method that has been tested at ORNL.

Understanding the effect of global change on the environment will continue to be a high-profile need.

groundwater are being developed. For instance, in situ vitrification at ORNL and deep-soil mixing with vapor removal of organics at Portsmouth draw heavily on a healthy blend of earth and engineering sciences. The importance of such cost-effective applications, coupled with expanded computer capabilities for improved decision analysis, cannot be overlooked in an era of tight budgets in the restoration world.

A significant milestone was reached with the updated mapping of the Oak Ridge Reservation, confirming that it has the most complex geology (and resulting hydrology) of any DOE site nationwide. This, coupled with high rainfall, an active groundwater–surface water system, long use of diverse disposal methods, and a nearby population center, makes the restoration challenges at Oak Ridge the greatest in the DOE system. Partially as a result of this complexity, a company-wide Groundwater Program Office was formed in the early 1990s; it is unique within the DOE system because it provides highly technical guidance on remediation and groundwater issues for five sites. Other new initiatives included data management for atmospheric studies (Atmospheric Radiation Program) and biogeochemical studies (Data Archive Center).

ESD now has a large cadre of earth scientists, including 75 who hold graduate degrees, reflecting a steady growth since 1972. Over the years, the emphasis on earth sciences has changed from soil science to more geochemistry, hydrology, and applied engineering sciences. Activities of ESD earth scientists are spread across the United States and in many foreign countries.

Overview

The earth sciences have played a key role in the evolution of ORNL, although their role has often been behind the scenes. As for the earliest use of earth science principles in waste disposal and the attitudes of some of the earliest scientists toward disposal of liquid waste, there is a greater story to be told —one that deserves more investigation. Indeed, earth science principles actually were involved in the original decision to site part of the Manhattan Project in Oak Ridge. The abundance of surface water and electricity (from hydroelectric plants), the topography that allowed each facility to be placed in a separate valley (to help isolate accidental releases), and inexpensive land (poor farm land because of topography) were among the reasons this site was selected.

Even in these uncertain times (remember 1963?) opportunities for the earth sciences are many, and these should be clarified. Certainly, efforts to meet the environmental restoration needs of DOE (and DOD) will draw heavily on this discipline, and innovative ways to blend basic research with applied programs are paramount. Understanding the effect of global change on the environment will continue to be a high-profile need, and there will be more attention on earth resources, especially water. Increased interactions among earth scientists and engineers across the ORNL complex seem essential at this time. All earth scientists are familiar with James Hutton's principle of uniformitarianism: "the present is the key to the past." We must look toward the future, however, and draw on another phrase that, at least, partially summarizes the situation: others' sins of yesterday are the key to our tomorrows.

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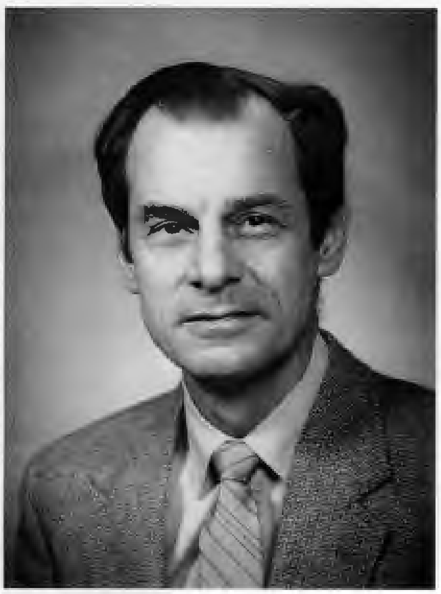
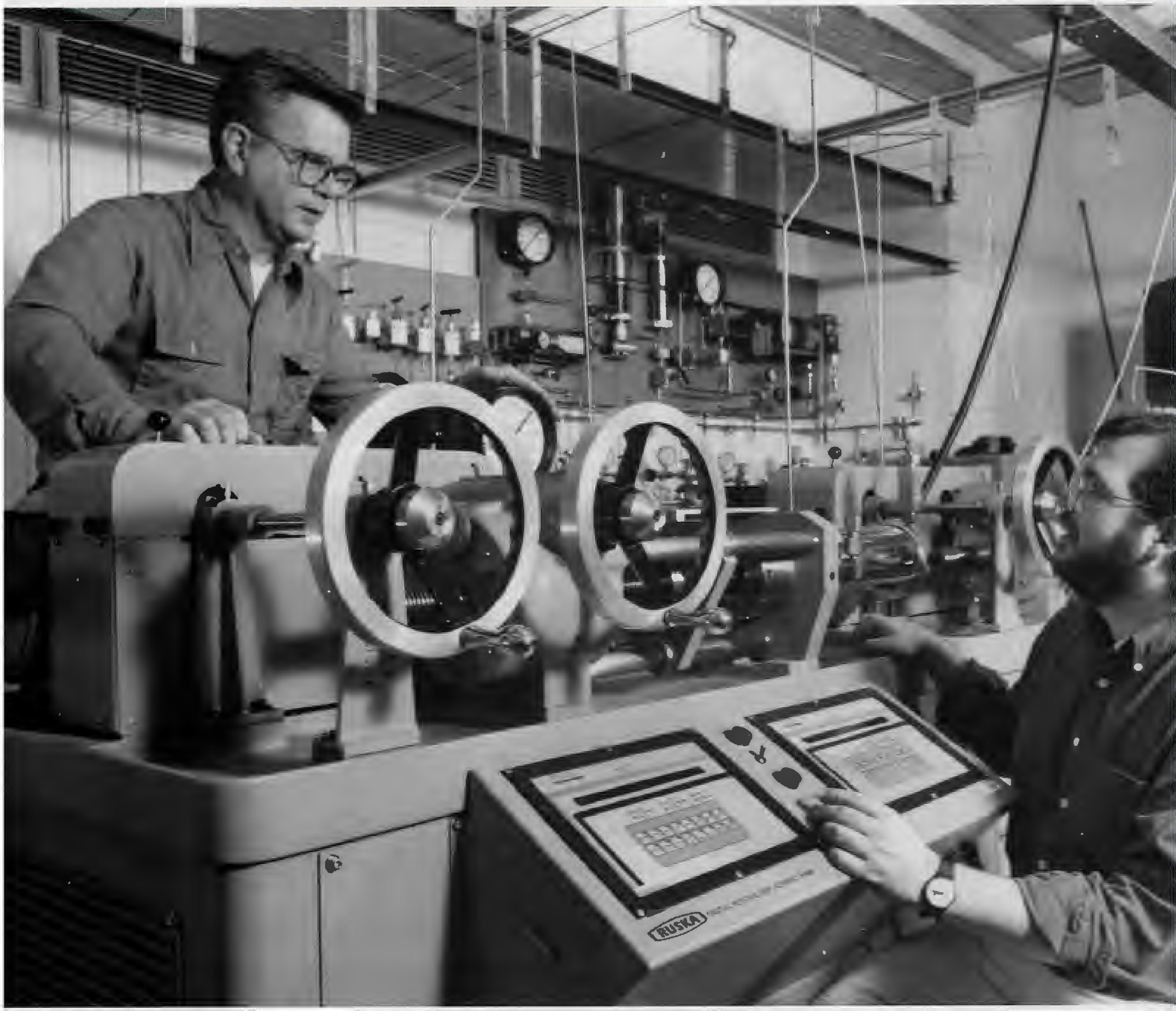
BIOGRAPHICAL Sketches

STEPHEN H. STOW is the program manager of Environmental Management for ORNL's Environmental Sciences Division (ESD). From 1988 to 1995, he was head of ESD's Earth and Atmospheric Sciences Section. After joining the ORNL staff in 1980, he became program manager for the Laboratory's Waste Isolation Program and the Sedimentary Rock/Geoscience Technology Support Programs. A graduate of Vanderbilt University, Stow has a Ph.D. degree in geochemistry from Rice University. Before coming to ORNL, he worked as a research scientist for Continental Oil Company in Ponca City, Oklahoma, and as a professor of geology at the University of Alabama at Tuscaloosa, where he was also on staff with the U.S. Bureau of Mines. He has also served as a private consultant for geologic waste disposal and minerals exploration. He has been chairman of the International Commission on Hazardous Wastes (International Association of Hydrogeologists). He served as the program leader for development of the "natural system" portion of the new DOE-American Nuclear Society International Conference on High-Level Radioactive Waste Disposal. He has been active in science education initiatives in many earth science societies. He is a fellow of the American Association for the Advancement of Science and of the Geological Society of America.



Hot Water, Hot Rocks, *Hot Science*

By David J. Wesolowski



Jim Blencoe (left) and DOE Distinguished Postdoctoral Fellow Jeff Seitz (seated) "man the pumps" on ORNL's vibrating-tube densimeter, a facility that operates on the principle of a tuning fork. It enables geochemists to measure densities of fluid mixtures up to one part per million at temperatures up to 400°C and pressures up to 4000 atmospheres.

Of the numerous energy sources, several important ones come from deep inside the earth. Coal, oil, and natural gas have formed over time through the interaction of enormous pressures and temperatures on organic material. Geothermal energy—steam and hot water—is also a product of these subsurface forces. Even the raw material for nuclear energy, uranium, comes from ores deposited by hot water circulating through the earth's crust. ■ Geochemists in ORNL's Chemical and Analytical Sciences Division (CASD) focus on developing experimental and analytical methods to investigate and quantify the natural processes occurring below the surface. This earth science research examines processes that influence hydrocarbon and geothermal energy development, nuclear and toxic waste migration, and elemental cycling in the ocean-atmosphere-lithosphere system—research relevant to human use of the earth's energy and material resources. ■ The roots of geochemical research at ORNL reach all the way back to the late 1940s, when pioneering studies of the properties of high-temperature water and salt solutions were conducted in the old Reactor Chemistry Division. These seminal contributions, spanning more than four decades, were made by physical chemists Bill Marshall, Charlie Baes, Milt Lietzke, Arvin Quist, Fred Sweeton, Dick Busey, Howard Holmes, and many others. Their work has been continued by Bob Mesmer (leader), Don Palmer, Mike Simonson, Patience Ho, and Mirek Gruszkiewicz, all of the High Temperature Aqueous Chemistry Group. These scientists have firmly established ORNL as one of the world's leading centers for experimental studies of the properties of hydrothermal fluids, including water and steam used to generate energy in fossil and nuclear power plants. It was inevitable that a geoscience research program would grow from this fertile ground because water is the ubiquitous, premier solvent and transporter of matter and energy in the earth's crust.

ORNL is one of the world's leading centers for experimental studies of the properties of hydrothermal fluids.

ORNL is home to a world-class program in geochemistry.

Hydrothermal Geochemistry

Basic hydrothermal geochemistry research in Bob Mesmer's group began formally in 1975 and grew at a steady pace to a half-million-dollar per year program by 1984. It has been supported by DOE's Office of Basic Energy Sciences, Geoscience Research Program and the Division of Geothermal Technology Development. The group was able to determine precisely the acid-base properties of water in geothermal brines and the thermodynamics of dissolved silica species (the major component of geothermal reservoir rocks) at temperatures up to 300°C. They used unique systems developed by Mesmer and his colleagues for measuring acidity levels (pH) at high temperatures. Because another very important earth fluid, silicate magma, provides the primary heat source for geothermal energy resources, the Chemistry Division's first bona fide geochemist, Mike Naney, was hired in 1978 to study its properties. He was joined in the early 1980s by geochemists Ed Drummond, Frank Dickson, Dave Cole, Jim Blencoe, and me.

The Geochemistry Group was hatched from Mesmer's group in 1985. It was placed under the leadership of Ed Drummond, who has since left us for the more lucrative field of real estate development in Knoxville. Since 1989 I have had the great privilege of being the leader of this group, which includes Jim Blencoe (see photograph on p. 86), Dave Cole (see photograph on p. 89), and a number of visiting scientists, graduate students, postdoctoral fellows, and research faculty members at the University of Tennessee, Knoxville. It is interesting to note that Drummond, Cole, and I, as well as Gary Jacobs [head of the Earth and Engineering Sciences Section in the Environmental Sciences Division (ESD)], were fellow students together in the Geosciences Department at Pennsylvania State University at the same time that Jim Blencoe was a member of the faculty. We often call ORNL "Penn State South." Just to show how small the world is, Steve Stow (author of the previous article in this issue) was Drummond's master's thesis advisor at the University of Alabama!

Although the Geochemistry Group maintains strong ties to its past, its activities have broadened greatly in recent years. Much of my work involves continued collaboration with chemists Don Palmer and Bob Mesmer in experimental studies of the thermodynamic and kinetic properties of reactions and dissolved species in hot water, often using modified versions of the same high-temperature pH cell that Mesmer developed 26 years ago. We try to identify and study in detail aqueous reactions that have a controlling influence on subsurface solution chemistry; the solubilities and sorptive properties of minerals and waste forms; the stabilities of natural and man-made organic compounds in aqueous solutions; and permeability changes and reservoir characteristics in hydrocarbon, geothermal, and groundwater systems.

Stable Isotope Abundances

Dave Cole is one of the world's leading experts in the study of geochemical controls on the relative abundances of the naturally occurring stable isotopes of oxygen ($^{18}O/^{16}O$), hydrogen (D/H), carbon ($^{13}C/^{12}C$), and sulfur ($^{34}S/^{32}S$) in minerals and fluids. These isotope ratios provide a wealth of information on the fluid sources and time-temperature histories of fluid-rock interactions in geological systems. Using state-of-the-art analytical facilities and a wide array of hydrothermal pressure vessels suitable for operation at temperatures up to 400°C and pressures up to 4000 atmospheres, Cole and his colleagues investigate the kinetics of isotope exchange reactions and the equilibrium partitioning of isotopes between brines and other phases, including minerals and steam.

Cole is also interested in the natural distributions of these isotopes in real rocks and fluids. He published a paper recently in *Nature* in which he and collaborators at New Mexico State University used the oxygen and carbon isotope ratios in desert soil carbonates (calcium carbonate, or "calcite"—$CaCO_3$) to suggest that a major increase in atmospheric carbon dioxide some 9000 years ago may have resulted in a shift in plant communities of the southwestern United States from grassland to desert scrub. This research finding suggests that future productivity of certain food crops could decrease as carbon dioxide levels in the atmosphere continue to rise.

Probing Conditions Throughout Earth's Crust

Jim Blencoe has successfully completed development of two unique facilities that were initially conceived by Mike Naney and Ed Drummond. Our internally heated pressure vessel (IHPV) is capable of operation at pressures up to 10,000 atmospheres and temperatures up to 1200°C, conditions similar to those encountered at the base of the earth's crust. Blencoe and his colleagues are using this system to determine the thermodynamic properties of granite melts and coexisting aqueous fluids in a project funded by DOE's Office of Geothermal Technology Development. They also use the unique capabilities of the IHPV to study the properties of fluids containing water, carbon dioxide, methane, and nitrogen at high temperatures and pressures.

Blencoe and his co-workers greatly enhance these types of studies by using our newly developed vibrating-tube densimeter, which allows them to measure the pressure-volume-temperature relationships of fluid mixtures at temperatures up to 400°C and pressures up to 4000 atmospheres at unprecedented levels of accuracy. This work is contributing enormously to our current understanding of the behavior of natural gas in hydrocarbon reservoirs and gas pipelines, and the influence of natural fluids on geological processes.

New Analytical Capabilities

In addition to the experimental studies described here, the recent creation of CASD by merging the former Chemistry Division and Analytical Chemistry Division has further enhanced longstanding efforts to develop unique analytical capabilities for application in the earth sciences. Geochemist Lee Riciputi, who joined CASD's Inorganic Mass Spectrometry Group in 1991, has been helping the group use its unique capabilities to detect and measure concentrations of trace elements and radiogenic isotopes in rocks and soils for DOE's earth science missions. He is also collaborating extensively with members of the Geochemistry and Secondary Ionization Mass Spectrometry (SIMS) groups in the application of ion microprobes for studies of the distribution of trace elements and stable isotopes in rocks and minerals at the spatial resolution of individual mineral grains. This technique has been successfully employed to determine the origins of hydrogen sulfide-bearing, or "sour," natural gas in major hydrocarbon reservoirs. It has also been used to determine the partitioning of oxygen isotopes between water and magnetite, a natural iron oxide found in oil and gas fields as well as corroded power plant boilers. Finally, this approach proved useful in tracking the distribution of radioactive cesium and strontium in a recent ORNL test of in situ vitrification, a method of isolating and immobilizing radioactive waste at a burial site, in collaboration with Mike Naney and Gary Jacobs of ESD (see the preceding article by Steve Stow). Currently, Riciputi is working with Pete Todd and Tim Short of the SIMS Group, with support from the Laboratory Director's R&D program, to develop a unique ion microprobe specifically designed for high-precision stable isotope ratio measurements in rocks and minerals.

Dave Cole prepares a carbon dioxide gas sample extracted from soil carbonates from the southwestern United States for analysis of its $^{13}C/^{12}C$ and $^{18}O/^{16}O$ ratios in an ORNL mass spectrometer. He will use this information to assess the effects of rising atmospheric carbon dioxide content on plant communities some 9000 years ago.

A large number of other basic and applied research and development activities within CASD have direct application in the earth sciences. To mention just a few: Gary Van Berkel of the Organic Mass Spectrometry Group has developed sophisticated analytical methods for detecting geoporphyrins, a class of "biomarkers" that indicate the biological origins of organic material in petroleum source rocks. Jack Young of the Optical Spectroscopy Group has collaborated with Larry Robinson of the Neutron Activation Analysis Group to determine whether dinosaur bones contain elevated concentrations of iridium, which might prove that their extinction was related to a large meteorite impact. The Analytical Methods and Environmental Monitoring groups have pioneered the development of instrumentation for subsurface soil gas analysis. Also, the Physical Organic Chemistry Group has for many years been studying the molecular properties of coal and related organic compounds.

CASD is home to a world-class program in experimental chemistry and geochemistry. The program provides the fundamental information needed to formulate accurate predictive models for the discovery of energy and material resources, development of these resources, and analysis of the consequences of their use. This work is enhanced by a parallel program to develop new analytical methods and instrumentation that will enable us to monitor geological processes more accurately or observe them in new ways. These capabilities will no doubt stand us in good stead as we move into the next century.

BIOGRAPHICAL Sketches

DAVID J. WESOLOWSKI was leader of the Geochemistry Group in ORNL's Chemical and Analytical Sciences Division until recently when David Cole succeeded him. He is also the Laboratory's coordinator of Geosciences Research Programs, which are supported by DOE's Office of Basic Energy Sciences. A native of Canonsburg, Pennsylvania, he holds a Ph.D. degree in geochemistry and mineralogy from Pennsylvania State University. He has worked as an assistant geologist with the U.S. Bureau of Mines and exploration geologist for U.S. Steel Corporation. He joined ORNL's Chemistry Division in 1983 as a Eugene P. Wigner Fellow and attained his present position in 1989. Wesolowski serves as secretary of the Geochemical Society and is an associate editor of the society's international journal *Geochimica et Cosmochimica Acta.* He is an adjunct professor in the Department of Geological Sciences at the University of Tennessee at Knoxville, where he has taught graduate courses in aqueous and stable isotope geochemistry.

AWARDS & APPOINTMENTS

Bill R. Appleton

Fred E. Bertrand

Frances E. Sharples

Thomas J. Wilbanks

Bill R. Appleton has been named associate director for Advanced Materials, Physical, and Neutron Sciences (AMPNS), a new directorate that consolidates the former Physical Sciences and Advanced Materials and the Advanced Neutron Source directorates. **James B. Ball** is the deputy associate director for AMPNS.

Fred Bertrand has been named director of ORNL's Physics Division, succeeding **James B. Ball**.

Colin West has been named leader of ORNL's new Neutron Sciences Program Office.

Jackson B. Richard has been named director of the new Office of Laboratory Nuclear Operations, which addresses matters relating to safety, operation, maintenance, and support of nuclear facilities at ORNL.

Frances E. Sharples has been appointed deputy director of ORNL's Center for Risk Management. She is also head of the Environmental Analyses Section of ORNL's Environmental Sciences Division.

ORNL Director Awards for 1995 were presented by ORNL Director Alvin Trivelpiece to the **Solid State Division, Chemical Technology Division,** and the **Office of Radiation Protection**.

James B. Roberto has been elected vice chair of the Division of Materials Physics of the American Physical Society.

Michael B. Farrar has been named the first manager of ORNL's High Flux Isotope Reactor Facilities Upgrade and In-Service Inspection Project.

Lisa Stubbs has been named a member of the DOE Human Genome Coordinating Committee.

Robert B. Cook has been named an associate editor of the journal *Biogeochemistry*.

Dr. James E. Phillips has been appointed director of ORNL's Health Division.

Yousry Y. Azmy has been selected to receive the American Nuclear Society's 1995 Young Member Engineering Achievement Award.

Edgar Laracurzio has been named secretary of the Subcommittee on Ceramic Matrix Composites of the American Society for Testing and Materials.

A 1995 Chrysler Neon that won the championship in the 1995 Hybrid Electric Vehicle Challenge was tested at **ORNL's Buildings Technology Center** before entering the national performance and acceleration competition in Auburn Hills, Michigan. The car, which operates on natural gas and electricity as alternative energy sources, was altered and tested by 40 engineering students at the University of Tennessee at Knoxville.

Thomas J. Wilbanks recently received the James P. Anderson Medal of Honor in applied geography from the Association of American Geographers. This award is the highest honor bestowed by the profession of geography in recognition of distinguished service in applying geographic knowledge and perspectives to real-world issues. Wilbanks was cited for his contributions as an international leader in the field of energy problem solving for developing countries.

Patrick J. Mulholland has been named chair of the Executive Committee of the North American Benthological Society and has received the Distinguished Alumni Award of the Department of Environmental Sciences and Engineering of the University of North Carolina at Chapel Hill.

Colleen Marie Dunnigan Mattison has been named director of the Ecological and Physical Science Study Center in ORNL's Office of Science Education.

S. Y. Lee has been appointed general chairman for the 33rd annual meeting of The Clay Minerals Society to be held in June 1996 in Gatlinburg, Tennessee. Its theme is "Clays in and for the Environment."

John S. Wassom has been appointed to chair two committees of the Environmental Mutagen

W. Harvey Gray

Virginia Dale

Tommy Wright

Steve Lindberg

Society: the Communications and Archives Committee and the Technical Committee. He has also been reappointed as a managing editor of the journal *Mutation Research*.

W. Harvey Gray has been named director of the Computational Center for Industrial Innovation at ORNL, a new DOE user facility.

Sokrates T. Pantelides has been named a distinguished visiting scientist at ORNL.

Robert Hawsey, director of the Superconductivity Technology Center at ORNL, recently received the Gold Medal in the Lang-Rosen Award series from the *Journal of Technology Transfer*.

Virginia Dale has been elected member at large to the governing board of the Ecological Society of America.

Nic Korte has been named a member of a Federal Interagency Assessment Team on oxygenated fuels.

Tommy Wright was recently elected a fellow of the American Statistical Association.

Laura Toran has been named a member of the committee to select outstanding students papers for the Hydrology Section of the American Geophysical Union.

Robert Siegrist was selected as a NATO fellow for two years; he is focusing on in situ remedial technologies. **Siegrist, Dianne Gates,** and **Robert Cline** recently placed first in a poster presentation for the Water Environment Federation's 67th Annual Conference.

According to *Science Watch* and *Current Contents* magazines, **Steve Lindberg** is author of one of the Top Ten Hot Papers in Ecology and Environmental Sciences published since 1981. His paper was ranked sixth in total citations and tied for second in average citations per year since published. Lindberg's paper, "Atmospheric Deposition and Canopy Interactions of Major Ions in a Forest," coauthored with Gary Lovett, Dan Richter, and Dale Johnson, was published as a cover article in a January 1986 issue of *Science*. **Lindberg** also has been appointed to the editorial board of the international journal *The Science of the Total Environment*.

Richard J. Norby has been elected a fellow of the American Association for the Advancement of Science.

ORNL's **High Flux Isotope Reactor (HFIR)** has received an award from the Nuclear Utilities Service (NUS) for having the most highly rated procedure program among all nuclear reactors at U.S. government facilities.

Ralph Turner, an ORNL mercury expert, has received a one-year fellowship from the National Research Council to conduct research at the U.S. Environmental Protection Agency's Environmental Research Laboratory in Gulf Breeze, Florida.

ORNL brochures and features, written by **Sybil Wyatt** and **Jon Jefferson**, received eight awards in the Southern regional competition of the International Association of Business Communicators. The winning entries are *Pioneer Women*, award of excellence, in the category of printed communication, booklets; "At the Speed of Light," a feature article in *ORNL '95*, award of excellence in the category of writing, long features; *Strength at the Core: The Core Competencies of Oak Ridge National Laboratory*, award of merit in design; "By Whatever Means Necessary" from the brochure on diversity at ORNL, award of merit in writing, personality profile; "War and Remembrance" from the diversity brochure, honorable mention in writing, personality profile; *ORNL '95*, honorable mention in printed communication, brochures.

Lynn Boatner, Stan David, and former graduate students **J. P. Sipf** and **D. P. Corrigan** received the "Best Poster Award" at a recent ASM International meeting for their paper "Solidification Microstructures in Single-Crystal Stainless Steel Melt Pools." It was presented in the form of a poster at the 4th International Conference on Trends in Welding Research.

New User Facility Measures Up

Some of the best and most precise measurement instruments in the world are now available to representatives of industry and universities, thanks to a new Department of Energy user facility at ORNL.

ORNL's Instrumentation and Controls Division has created the Metrology Research and Development Laboratories facility. It is one of more than a dozen DOE user facilities at ORNL that are open to the Laboratory's more than 4000 yearly guest researchers.

"Small companies in the area need to use certain testing equipment they can't afford to buy," says Tim McKnight, engineer at the user facility. "We have made this facility available because it enables these companies to expand their capabilities by using our instruments."

Large companies from around the nation also benefit from the facility, says Jim Hylton, group leader of the I&C Division's Sensors and Metrology Group. They have access to unique instruments at the facility, which consists of an array of research centers for developing and testing measurement and sensing technologies. Facility instruments can measure temperature; flow rate for liquids and gases; light intensities and diffraction; and levels of electromagnetic, acoustic, and ionizing radiation.

One unique instrument available is the gravimetric calibrator, a state-of-the-art device that can measure flow rate of any type of gas. Built for use by the semiconductor industry, it has been awarded an international patent and an R&D 100 Award, which is presented annually by *R&D* magazine in recognition of the year's most significant technological innovations.

Outsiders may also value ORNL's capability of measuring electrical noise that might interfere with operation of electronic systems. Such testing can be done on user equipment in the ORNL facility or at the user's outside facility using portable monitoring equipment loaned by the Laboratory.

ORNL also has a facility in which a user can expose equipment to harsh industrial environments for long-term tests. Such experiments can be controlled remotely over the Internet.

The Metrology Research and Development Laboratories not only provide a wide array of instruments but also offer more than 40 years of expertise to users.

"The users," Hylton says, "have access to the I&C Division's research and development staff of more than 100 scientists and engineers who specialize in diverse areas of measurement and sensor technology."

In addition to meeting the measurement and testing needs of today, McKnight says, the new user facility is developing the measurement and testing techniques of tomorrow.

"The facility's goals are to continue to provide state-of-the-art capabilities to industry and academia and to continue to improve the facility," he says. "We will continue to make ORNL-developed technology available to companies and universities."

—*April Davidson*

It is one of more than a dozen DOE user facilities at ORNL that are open to the Laboratory's more than 4000 yearly guest researchers.

At the Metrology Research and Develpment Laboratories facility, mechanical engineer Ruth Anne Abston prepares a mass flow controller for testing by ORNL's prize-winning gravimetric calibrator, which measures gas flow rates.

ORNL Wins Five R&D 100 Awards

ORNL's award-winning magnetic spectral receiver was developed by (from left) Steve Kercel, Robert Rochelle, and Mike Moore. It provides low-cost, highly accurate magnetic field monitoring in facilities where sensitive instruments are used. *Photograph by Bill Norris.*

ORNL researchers received five R&D 100 Awards in 1995, bringing the Laboratory's total of these awards to 79. The awards are presented annually by *R&D* magazine in recognition of the year's most significant technological innovations.

ORNL has received 79 R&D 100 Awards since the competition began.

Four awards were for research performed exclusively at ORNL, and the fifth was for a joint entry with 3M Company of St. Paul, Minnesota.

The awards were for the following processes or inventions:

- **Exo-Melt™ process.** This process provides a furnace-loading method for low-cost manufacturing of advanced materials such as nickel aluminide and iron aluminide. The Exo-Melt™ process requires less energy and time than conventional aluminide-producing methods. For details, see the article "Nickel Aluminides: Breaking into the Marketplace" on p. 4.
- **Gelcasting.** This new ceramic-forming process makes high-quality, complex-shaped ceramic parts and forgiving process" that can be quickly adapted for new materials and new applications. For more details, see the article "ORNL's Gelcasting: Molding the Future of Ceramic Forming?" on p. 24.
- **3M Ceramic Composite Filter.** This fiber-reinforced ceramic composite candle filter removes particulates from hot gas streams in pressurized fluidized bed combustion systems and coal gasification plants. Advantages over conventional filters include lower weight, lower pressure drop, enhanced thermal shock resistance, enhanced chemical stability, and easier cleanability. For more details, see Technology Transfer" on p. 124.
- **Magnetic spectral receiver.** This instrument monitors magnetic fields that can affect the function and accuracy of instruments used in a variety of applications, including nuclear power plant control rooms. The receiver provides low-cost, highly accurate magnetic field monitoring in diverse facilities whose operations rely on instrumentation. For more details, see the item on the facing page.
- **Gravimetric gas flow calibrator.** This device provides for accurate

calibration of gas flow meters with corrosive or noncorrosive gases. It is significantly more accurate than existing volumetric calibrators, many of which can operate only with nonreactive gases. The gravimetric gas flow calibrator uses a unique, patented technique for safe, automated, in-process weighing of gases. The device was originally developed for the semiconductor industry, which requires accurate instruments to calibrate mass flow controllers. These controllers regulate the flow of tiny amounts of various gases into vacuum chambers where semiconductors are produced. Other applications of the gravimetric gas flow calibrator are likely. For more information, see the item on p. 96.

Protecting Against Electromagnetic Interference

Ship captains have relied on compasses responding to the earth's magnetic field to guide them safely on their voyages. However, operators in nuclear power plant control rooms have found that magnetic fields can make their sensitive instruments less reliable.

To address this problem, ORNL researchers have developed an instrument to detect electromagnetic interference (EMI) caused by magnetic fields. EMI can cause disruptions in some of the high-performance digital control systems in nuclear power plant control rooms and in industries using similar sophisticated instrumentation.

The ORNL device, called the magnetic spectral receiver, provides low-cost, highly accurate monitoring of magnetic fields in diverse facilities where instrumentation is vital to their operation. By knowing the exact levels of EMI present, design engineers can more accurately specify the amount of EMI resistance required to protect sensitive instruments. To be safe, engineers typically call for greater EMI resistance, or "hardness," than is actually needed. Using more shielding than necessary, for example, is extremely costly and wasteful.

The ORNL device can detect electromagnetic interference in nuclear power plant control rooms.

"EMI resistance is achieved primarily by adding shielding," says Steve Kercel, principal inventor of the magnetic spectral receiver, which received an R&D 100 Award this year from *R&D* magazine. "However, other elements affecting EMI hardness are physical layout, proper termination of cables, and the judicious selection of software algorithms.

"The big issue is that all measures intended to improve EMI resistance are expensive, and it is desirable to use the least that you can get away with and still have the system work properly. Experts estimate that proper knowledge of ambient EMI would allow designers to save half the cost of digital instrumentation and controls packaging."

The magnetic spectral receiver, which at 65 pounds is portable, is one of the world's first devices that uses the wavelet transform, a processing system that provides analysis of transient, or very brief, effects that conventional receivers miss. Instead, these receivers treat the transient peaks as an EMI average, which fails to tell the whole story.

"It's similar to driving 100 miles per hour for an hour and then driving 30 miles per hour for an hour," Kercel says. "Your average speed is 65, but that number doesn't really paint an accurate picture."

Another advantage of the magnetic spectral receiver is its low cost. Although conventional EMI receivers cost up to $75,000, the ORNL unit would cost about $8000 when produced in reasonable quantities. One reason that other receivers cost more is that they provide high precision, resolution, and dynamic range. However, these capabilities are not needed for ambient surveys. In addition, the magnetic spectral receiver requires no attendant, considerably reducing labor costs over the typical 3-week monitoring period.

Although the magnetic spectral receiver is primarily intended for nuclear power plant control rooms, Kercel also expects it to be used by the textile and semiconductor fabrication industries. "Both industries suffer seemingly inexplicable failures of digital control equipment and suspect ambient EMI as the culprit," Kercel says. Companies in both industries have expressed interest in the receiver.

The same basic technology used in the magnetic spectral receiver could be modified for use in real-time environmental monitoring, surveillance, detection, and signature identification. In these applications the wavelet processor could be adapted to identify crucial features from the transient components of the signal. For example, Kercel says, by substituting a seismic transducer for the magnetic antenna and replacing a couple of other internal parts, the receiver could

Another advantage of the magnetic spectral receiver is its low cost.

be converted into a seismic monitor. The receiver can also be configured as a gunshot detector that would not be susceptible to other noises, such as thunder or vehicle backfires.

Other ORNL researchers who developed the award-winning receiver are William Dress, Robert Rochelle, and Michael Moore.—*Ron Walli*

Calibrator Measures Flow Rate of Corrosive Gases

Normally, measuring flow rates of corrosive and toxic gases takes several days. But anyone using the new calibrator developed by ORNL researchers can complete the task in only a few minutes. Flow rate is measured by weighing corrosive gases accumulating at volume rates as low as a few cubic centimeters per minute.

The gravimetric gas flow calibrator is a new type of gas flow calibration device that measures how fast any type and quantity of gas flows through gas flow meters, according to Carl Remenyik, the ORNL researcher who developed the device. By measuring the flow of gas in a minute, scientists can ensure that the gases, no matter how small an amount, are being discharged in precise doses during semiconductor manufacturing processes.

"The calibrator is significantly more accurate than other volumetric devices, many of which can operate only with nonreactive gases," says Remenyik, an engineer in the Instrumentation and Controls Division. "Strongly reactive gases eat away at most metals, but the calibrator is made of a stainless steel that will resist attacks. It will operate with almost any type of gas or vapor, and its accuracy is not affected by chemical reactions, condensation, or adsorption taking place inside."

Accurately weighing small quantities of flowing gas is difficult, says Remenyik. Most methods determine the weight of gas by measuring it on a balance that requires a long time to collect samples or by deriving it from equations relating temperature, volume, and pressure. Measuring temperature,

ORNL's award-winning gravimetric gas flow calibrator, which was developed by Carl Remenyik (shown here), provides for accurate calibration of gas flow meters with corrosive or noncorrosive gases. The calibrator was originally developed for use in the semiconductor industry, but Remenyik expects it to have several other applications. *Photograph by Bill Norris.*

volume, and pressure are indirect mass measurement methods that will have some errors that accumulate in the calculations.

"Because this calibrator does not depend on calculation of the gas density from pressure and temperature measurements," Remenyik says, "it is fundamentally more accurate than volumetric devices."

Also, balances that can measure 50- to 100-pound objects, the weight range of most gas containers, cannot accurately measure a few tenths of an ounce of gas inside the container. Scientists usually must spend hours or days collecting gas heavy enough to be weighed. Chemical reactions and adsorption significantly reduce the accuracy of indirect methods that derive the gas weight.

In the semiconductor industry, high-quality wafer chips require accuracy in the control of gas flow. Dozens of gases in small doses are used to manufacture semiconductor chips. The chips, which may be as small as the tip of a finger, are used in electronic devices, such as televisions, radios, and computers.

The ORNL calibrator, which won an R&D 100 Award from *R&D* magazine this year, uses a patented technique to measure the weight of gas. From a load cell balance, scientists suspend an empty vessel submerged in water to balance its weight by buoyancy. While submerged, the 50-pound steel container feels no heavier than one-tenth of an ounce. The container seems lighter because water pushes against objects, causing them to float like a log in a river. With a lighter calibration container, scientists can use a load cell sensitive enough to measure fractions of one-thousandth of an ounce. The flow rate is then determined by subtracting the weight of the empty, submerged calibration container from the weight of a calibrator filled with gas for 1 minute.

"The key to accuracy is the type of balance used to measure weight," Remenyik says. "Balances are made for a particular range of weight. A balance for weighing hundreds of pounds will not accurately weigh a few ten-thousandths of an ounce of a gas. This is why our technique is important. Because water takes away the bulk of weight, we can use the best balance available for accurate small measurements."

The calibration process begins and ends with the push of a button. In the first push, a valve seals off the normal path and reroutes the gas to an empty calibrator for a specific time interval, usually 1 minute. With the second push, the valve closes again and the gas continues to flow through the regular path. The test sample is then measured by the load cell. In the final push, the test sample is moved to an incinerator, where it is burned to harmless waste.

In addition to the semiconductor industry, gas flow calibrators can be used in standard laboratories and in other branches of the industry where gas flow controllers and meters are used. Funding for the gas flow calibrator was provided by ORNL's Metrology Program and the semiconductor industry.

—April Davidson

Restructuring a Mountain: Nature vs Human Intervention

Some of the land devastated by the May 18, 1980, volcanic eruption of Mount St. Helens is turning into a vast tree plantation. In other areas, native grasses and legumes are beginning to flourish. Fifteen years after the mountain blew, killing 85 persons and destroying property and natural ecosystems, it is taking on a life of its own.

Birds perch on dead, fully stripped tree trunks standing tall like telephone poles. Around the trees lie their fallen neighbors, strewn on the ground like pickup sticks by Nature's "blast from the past" method of instant logging. But nearby are newly planted Douglas fir trees and Pacific silver fir trees. Thanks to these fast-growing native trees and the return of grasses, wildflowers, and other natural species in other areas, tourists are now witnessing the "greening" of the once barren land around the mountain.

This rebirth amid death and destruction that marks the 15-year recovery of the Mount St. Helens ecosystem is of interest to scientists as well as tourists. Virginia Dale, a mathematical ecologist and associate director of ORNL's Environmental Sciences Division, has been studying plant recovery in the Mount St. Helens area since the eruption. She presented a paper on her findings on July 31, 1995, at the annual meeting of The Ecological Society of America in Snowbird, Utah.

Dale studied the devastation soon after the eruption and has since conducted a series of periodic surveys and analyses of the recovery. This year she completed work on her sixth survey of the region.

"Although it will take at least a century for the area to fully return to preeruption conditions," she says, "the data from the first 15 years show a strong and steady recovery.

The 1980 eruption, Dale says, created seven types of disturbances. They were the development of the crater, the flow of hot gases, the largest avalanche in history, a zone in which most trees were blown over, an area where needles were burned off the trees but the trees remained standing, ash deposits, and mud flows.

"My work is on the debris avalanche, which was one of the most heavily devastated areas," Dale says. "The recovery in each of the areas is unique."

The native species are surviving and growing even in the presence of the exotic ones.

View of a forest near Mount St. Helens 15 years after destruction by the volcano's eruption.

A native grass flourishes on the debris avalanche created by the 1980 eruption of Mount St. Helens (in the background).

Her studies suggest that human efforts to help the recovery have probably done more harm than good.

The Mount St. Helens National Monument was created in 1983 to protect 110,000 acres of the devastated area, which includes a pumice plain (pumice is lightweight volcanic glass full of cavities). This area is now left to recover in a natural manner.

"The rest of the devastated area—about 136,000 acres—is owned by the U.S. Forest Service, the state of Washington, or private owners," Dale says. "It is being actively managed largely for forestry. Plantations of two native species, Douglas fir and Pacific silver fir, will be harvested in about 60 years."

Dale notes that the area she studies is recovering from the eruption but still has a long way to go. In September 1980, the total number of plant species found in an area that suffered some of the worst devastation, the avalanche zone, was only 20. Her 1994 survey found 156 species of plants in the same area, much closer to the original 256 species found in the area before the eruption.

Her studies suggest that human efforts to help the recovery have probably done more harm than good. An immediate concern after the eruption was the possibility of massive erosion. To prevent it, the U.S. Soil Conservation Service, now known as the Natural Resources Conservation Service, planted nonnative, or exotic, grass and legume seeds (including bird's foot trefoil) in selected areas despite scientists' objections.

The concerns of these scientists were justified according to Dale's research. In the areas where these exotic seeds were spread, the nonnative plants thrived, slowing the return of the native species. However, Dale's recent surveys show that the tide has turned: the native species are surviving and growing even in the presence of the exotic ones.

For example, between 1983 and 1989, several species of trees, including the Douglas fir, declined in density in areas that had a large concentration of nonnative plants. But, between 1989 and 1994, the native trees in these areas are surviving and growing along with the exotic species.

"A dramatic effect of the exotic plants can be seen," Dale says, "but over time the native plants have done quite well at regaining their territory." Partly because of this experience, the Natural Resources Conservation Service now stocks its field stations with a variety of seeds native to each area.

Although the area still has a long way to go to achieve full plant recovery, Dale is encouraged by the progress she sees.

"In the absence of humans doing anything," she notes, "succession is occurring. And where humans did intervene, succession is also occurring, but just a bit more slowly."

—*Carolyn Krause*

Food Dye May Raise Risk of Breast Cancer

Eating foods containing a commonly used synthetic dye may raise a woman's risk of developing breast cancer, according to research conducted at ORNL and recently reported in the journal *Cancer Letters*. Synthetic food dyes are added to many foods and beverages to improve their appearance.

"Food dyes, pesticides such as DDT, and pollutants may be responsible for the increasing breast cancer rate among American women because they mimic the effects of the hormone estrogen," says Craig Dees, head of the Molecular Toxicology Group in ORNL's Health Sciences Research Division. "Some researchers have suggested that these so-called environmental estrogens may be helping to cause the worldwide decrease in human sperm counts and are the cause of reproductive abnormalities in animals. They also have natural estrogen's ability to attach to breast cells and order them to rapidly reproduce, a process that is required to cause cancer."

Using a new highly sensitive and specific test, ORNL researchers have found that Red Dye No. 3 is a "complete carcinogen" because it carries out the two actions that together cause cancer. First, it damages the DNA, or genetic material, in breast cells. Second, it gives cells the order to grow out of control—that is, divide more rapidly than normal. This second finding suggests that the synthetic food dye is an environmental estrogen. The research was supported by the Laboratory Directed Research and Development fund supported by DOE.

Dees says there is evidence that other food dyes may also damage DNA. But ORNL studies show that Red Dye No. 3 is more likely to cause breast cancer because it also issues an order for these cells to grow.

Americans' exposure to pesticides has dropped in recent years, according to a study by Curtis Travis, director of ORNL's Center for Risk Management. However, Dees says that today Americans eat food that may contain levels of synthetic food dyes that are at least 10 million times higher than the level of pesticides. Since 1979, he adds, the production of synthetic dyes for the food industry has increased 5% per year.

"The health risk of dyes may be rising because our diet is increasingly made up of processed foods that are more likely to contain food dyes," Dees says. "These foods include lunch meats, hots dogs, snack foods, and candies. Beverages also contain food dyes. Synthetic food colorants, like Red Dye No. 3, are less expensive than natural dyes, so use of these colorants is increasing."

One of eight women in the United States develops breast cancer, which annually kills almost 50,000 American women. Dees says a woman's risk of getting breast cancer may be linked to increased body fat, poor exercise habits, and a diet high in fat, and in perhaps 5% of the cases, to an inherited genetic defect. But he believes that environmental estrogens in food may play the most important role in the development of breast cancer.

"American women are approximately 5 times more likely to develop breast cancer than are women in less developed countries," Dees says. "Diet and lifestyle may explain this difference. When women from less developed countries adopt a westernized diet and lifestyle, their cancer risks equal those of women in the United States."

Dees and associate Don Henley determined that Red Dye No. 3 is a complete carcinogen by using a highly sensitive and specific technique called a gel mobility shifter assay. In one test, Henley extracted a naturally produced tumor suppressor protein (called p53) from breast cells exposed to Red Dye No. 3 as well as from breast cells exposed to other dyes and to DDT. Before it was extracted, the p53 protein had "sensed" that DNA in the cells exposed to Red Dye No. 3 had been damaged. Its response was to grab the DNA in a certain region to tell the cell to stop growing so that repairs could be made before the cell reproduced.

The extracted protein instead grabbed a radioactively labeled double strand of synthetic genetic material as part of the gel mobility shift test. This strand is identical to the genetic region to which the p53 protein normally binds within a cell. The strength or amount of the grabbing by the p53 protein caused the radioactive DNA to move very slowly and collect in one place in a gel subjected to an electric field (gel electrophoresis). This effect was revealed as a thick dark band on X-ray film laid over the gel, because the film is sensitive to radioactivity.

"The increased binding of p53 proteins to the synthetic genetic material was at least as high for cells exposed to Red Dye No. 3 as for cells treated with other DNA-damaging chemicals or exposed to radiation," Dees says. "We believe that the p53 proteins are trying to stop the breast cells from duplicating themselves after they are exposed to the red dye so that abnormal genetic material is not copied. If the p53 proteins are prevented from doing their job, then cells eventually grow out of control, leading to cancer."

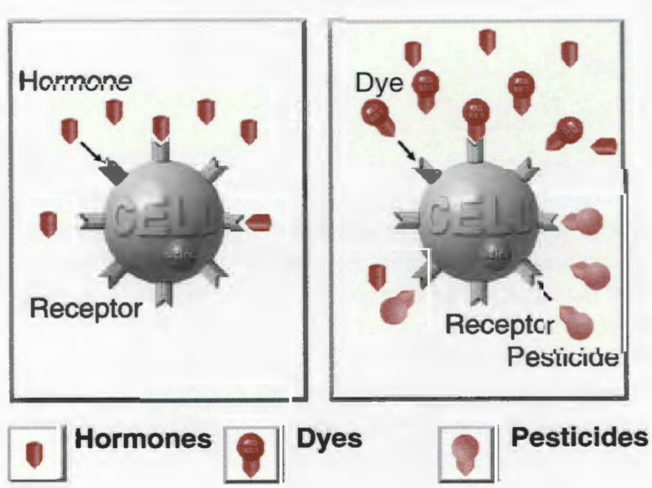
Using another gel shifter technique, Dees' associate Scott Garrett studied a synthetic DNA fragment that binds an estrogen receptor from a human breast cell. An estrogen receptor is a protein that is assembled in a breast cell after binding to an estrogen. Once a receptor is assembled in response to exposure to an estrogen or estrogenlike substance, it then attaches to specific sites in the DNA that tell the cell's nucleus to reproduce. Exposure to estrogen or Red Dye No. 3 could tell breast cells containing damaged DNA to proliferate.

For the gel mobility test, Garrett introduced a synthetic version of this DNA along with estrogen receptors produced in breast cells by exposure to Red Dye No. 3. The test showed that the newly formed estrogen receptors extracted from breast cells bind strongly to the synthetic DNA fragment in the gel. Thus, in addition to damaging DNA, Red Dye No. 3 is acting like an environmental estrogen by binding to estrogen receptors just like DDT.

"By binding the estrogen receptor, the dye is telling the cells to reproduce rapidly," Dees said. "This result suggests that exposure to Red Dye No. 3 could significantly increase the risk that breast cells become cancerous."

—Carolyn Krause

Red Dye No. 3, which is ingested by American women in large amounts, is capable of binding to the estrogen receptor and mimicking the natural hormone along with other environmental estrogens such as the pesticide DDT.



ORNL Probes Rapid Disappearance of Children's Fingerprints

Knoxville Police Detective Art Bohanan and ORNL's Michelle Buchanan examine fingerprints. Buchanan's research suggests that children's fingerprints don't last as long as adult fingerprints because of a difference in chemical composition.

Children's fingerprints contain more volatile chemicals, such as free fatty acids.

While investigating the abduction and murder of an East Tennessee girl, Art Bohanan, a specialist with the Knoxville Police Department, encountered a phenomenon that had perplexed him before. Although witnesses saw the child enter the suspect's car, none of her fingerprints could be found anywhere inside the vehicle.

The suspect initially confessed but later recanted, making the absence of the victim's fingerprints a hurdle for the prosecution. He was convicted, but for Bohanan, a veteran of several grim criminal investigations involving children, the case reinforced a previous hunch: kids' fingerprints don't stick around the way adults' do.

Bohanan found his observation surprisingly fresh. Calls to contacts in the Federal Bureau of Investigation (FBI), the National Institute of Justice, Scotland Yard, and even a police friend in Russia turned up no evidence that the problem had been considered, much less studied. A letter from the FBI referred to it as an "area that needs to be explored."

Bohanan described his problem in a telephone call to ORNL Director Alvin Trivelpiece, who gathered 10 ORNL researchers to propose a solution. After the detective met with researchers, Michelle Buchanan of the Chemical and Analytical Sciences Division began a project that, as Bohanan puts it, "could lead us to all kinds of things down the road."

Buchanan enlisted a willing group, ages 4 to 17, to shake vials of alcohol between their thumb and forefinger to collect chemicals from their skin. She also took similar, noninvasive samples from adults, ages 19 to 46. Undergraduate students Jennifer Fletcher of Auburn University, Matt Johnson of North Dakota State University, and Scott Shultz of Transylvania University conducted gas chromatography-mass spectrometry tests on the samples in Buchanan's lab. The results confirmed the detective's hunch: Kids' fingerprints are different.

"We see a marked difference in the chromatograms," Buchanan said. "Children's fingerprints contain more volatile chemicals, such as free fatty acids, probably because they haven't gone through puberty yet. Adult prints display longer-lasting, higher molecular weight compounds such as long-chain alkyl esters of fatty acids."

Knowing the chemical difference in adults' and children's fingerprints is likely to lead to a test for latent juvenile fingerprints. Buchanan said that as her organic mass spectroscopy group identifies the compounds in the prints, Tuan Vo-Dinh of ORNL's Health Sciences Research Division is developing a computational method to enhance the visualization of fingerprints. The fact that the gas chromatographic profiles identified so many chemicals present in the skin has Buchanan theorizing that the research could lay the groundwork for new noninvasive diagnostic procedures.

"It has been reported in the literature that a number of compounds present in the skin's surface are indicators of some diseases," Buchanan said. "We hope to improve sampling techniques to develop new methods to detect target compounds that can tell us more about what's going on inside the body."

Detective Bohanan, an inventor of a method for lifting fingerprints, enthusiastically envisions what his police work and ORNL's research could lead to in solving crimes. "Forensic evidence is often lost or tainted because of delays in analysis or accidents along the way," he says. "I would also like to see this evolve into skin patch drug tests that could be used on the scene." For Bohanan, the medical applications that could result would be an especially gratifying bonus from a scientific pursuit of such sad origins. *—Bill Cabage*

ORNL Technique Can Screen for Carriers of Cystic Fibrosis Gene

This is the first time that mass spectrometry has been used to diagnose a genetic disease by DNA analysis.

A new ORNL-developed technique that could be used to rapidly screen many people for the defective gene that causes cystic fibrosis (CF) has been applied by ORNL and the University of Tennessee Medical Center (UTMC). In a test of samples from 30 persons who have normal or defective forms of the CF gene, the technique was 100% accurate, as reported in the journal *Rapid Communications in Mass Spectrometry.*

CF is an inherited fatal disease caused by a genetic defect. About 4% of Americans, mostly Caucasians, carry a defective form of the gene, which makes it the most common genetic defect of its severity in the United States. About 40,000 people in the United States have cystic fibrosis.

People with the disease suffer from respiratory and digestive disorders. Because their lungs become covered with a sticky mucus that promotes infection by bacteria, many CF patients require frequent hospitalizations and continuous use of antibiotics and other expensive medications. The total cost of caring for a typical person with cystic fibrosis, who has a median life expectancy of almost 30 years, is estimated at $250,000.

Because each person with CF is the child of parents who both carry defective forms of a particular gene, there is interest in large-scale screening to let people know their chances of having a child with CF.

The rapid screening technique was developed by C. H. (Winston) Chen and Steve Allman, both from the Photophysics Group of ORNL's Health Sciences Research Division, in conjunction with L.-Y. Ch'ang, M Schell, and C. Ringelberg, all of UTMC's Graduate School of Medicine, Department of Medicine, and Dr. Karal J. Matteson, a CF expert at UTMC's Graduate School of Medicine, Department of Medical Biology. They were assisted by K. Tang, a graduate student from Vanderbilt University. Other collaborators at ORNL include Bruce Jacobson, Mayo Uziel, K. L. Lee, M. Docktycz, G. B. Hurst, Scott McLuckey, Michelle Buchanan, and Richard Woychik. The ORNL work was sponsored by the internally funded Laboratory Directed Research and Development Program.

"Our technique uses laser mass spectrometry," Chen said, "and this is the first time that mass spectrometry has been used to diagnose a genetic disease by DNA analysis. One advantage of this technique over conventional analysis by gel electrophoresis is speed—it's at least ten times faster because the whole procedure can be done in minutes, not hours. Another is that it does not use toxic chemical or radioactive materials, which require costly methods of disposal."

In this technique, laser mass spectrometry detects a common defect or mutation in the CF gene—the lack of key genetic material. The absence of three pairs of chemical bases in a specific region of the gene on chromosome 7 is responsible for 70 percent of cystic fibrosis cases. Chemical bases are the building blocks of DNA, the blueprint for life; the particular sequence and number of these bases, which vary from gene to gene, determine a gene's function in carrying out a life process or transmitting a trait to the organism's offspring.

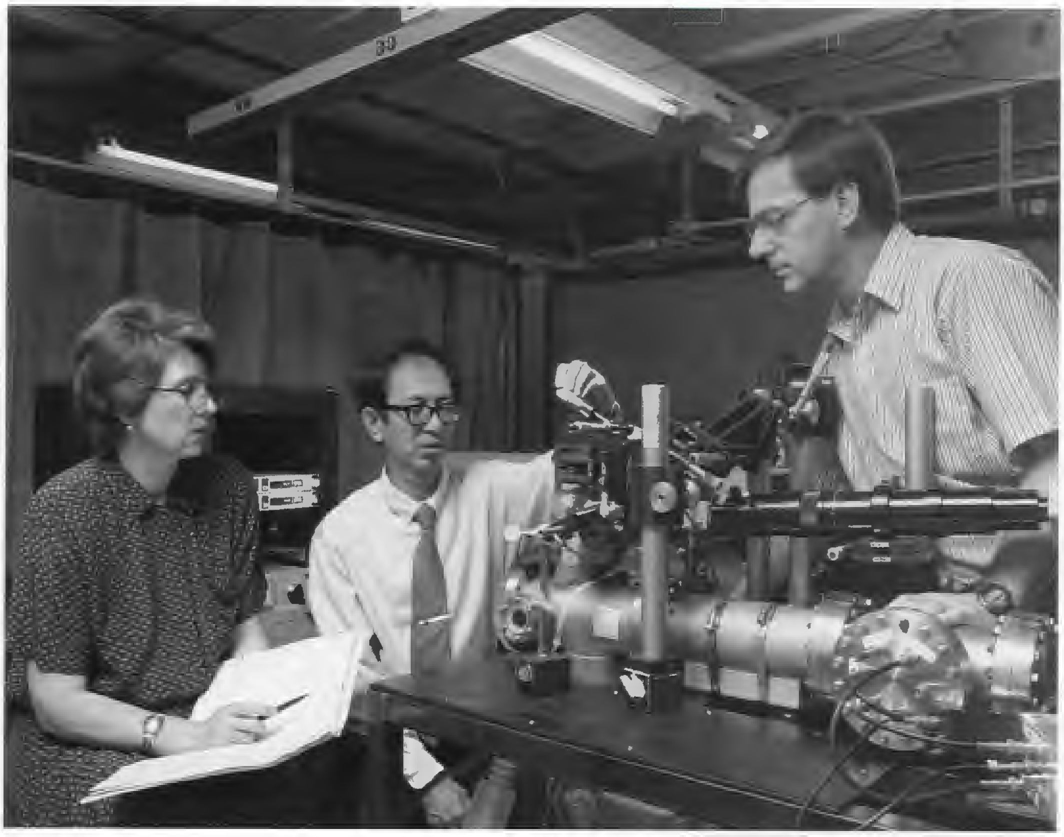
The causes of cystic fibrosis, long a mystery, are now becoming clear, thanks to advances in biology. Humans have a gene that manufactures a special protein—CFTR—that helps prevent the buildup of sticky mucus in the lungs. If the gene is defective, it causes cystic fibrosis.

Each gene is made up of two alleles, one from each parent. One correctly encoded allele of the CF gene is adequate for normal CFTR function. People who have a single defective allele are called carriers; they can pass the defect on to their offspring. Those with two defective CFTR alleles have cystic fibrosis.

If two carriers mate and have a child, the probability is 25% that the child will have cystic fibrosis. Thus, an accurate, fast screening technique would inform more couples of the likelihood that their future children would be born with CF.

The ORNL-UTMC technique can screen people to determine if they are normal, if they carry a defective CF allele, or if they have CF. For the experiment, the UTMC staff extracted DNA from human hair samples and isolated the part of each CF gene that would contain the known defect if present. They copied this segment millions of times using the polymerase chain reaction technique.

The UTMC staff sent to ORNL 30 samples, each a barely visible droplet, for a blind test. The ORNL scientists mixed each DNA segment with a chemical that absorbs laser light. The mixture was vaporized by ultraviolet light from a laser. The electrically charged DNA molecules formed in the vapor were detected in a time-of-flight mass spectrometer based on differences in size.



Nelli Taranenko, Winston Chen, and Steve Allman use the laser mass spectrometer to screen for the cystic fibrosis gene in a prepared hair sample.

Because the segments of defective CF genes have fewer chemical bases, they are smaller and lighter than the segments from normal genes. The gene segment that causes CF is even smaller than the segment with one defective allele. Since a lighter segment travels faster than a heavier one between the sample plate and detector, the three types of DNA segments can be distinguished by differences in time of travel.

These differences are displayed on a computer screen as spectra—lines with peaks and valleys. This information indicates whether a person has a normal gene, a totally defective gene, or a gene with a defective allele, making that person a carrier. ORNL's identifications of the 30 samples agreed completely with the results of conventional analyses.

—*Carolyn Krause*

Genes for Jeans: Engineered Enzyme Improves Fabric

Thanks to altered genes, it can stone wash jeans without stones and make them look better than ever. It can "eat" the paper wastes that occupy 40% of U.S. landfill space while removing ink from newspaper to make recyclable paper. It can convert wood to sugar, which can be turned into ethanol for fuel.

"It" is a new strain of bacteria discovered and altered by ORNL researchers. The altered bacteria rapidly produce cellulase, an enzyme used in fabric finishing detergents to smooth fabric, such as blue jeans, by removing puffy "pils" (knots that make cloth rough) from knitted material. Tests show that the bacterial enzyme produces a more attractive textile product than the commercially used acid cellulase fermented by fungi.

Craig Dees, a researcher in ORNL's Health Sciences Research Division who genetically altered the special bacteria, says that the bacterial enzyme has several advantages over the fungal enzyme. "The bacteria produce much more enzyme than

ORNL's bacterial enzyme can stone wash jeans, "eat" paper waste, and convert wood to sugar.

Craig Dees shows jeans stone washed conventionally by a fungal enzyme and jeans washed by a bacterial enzyme cellulase produced at ORNL. Tests show that the bacterial enzyme produces a smoother textile product with less backstaining by the colored dye than the commercially used acid cellulase fermented by fungi. *Photograph by Bill Norris.*

fungi can in the same time," he says. "There is less back staining, or smearing of the blue dye, on the white areas of the jean cuffs. The bacterial enzyme can withstand a wider range of acidity levels and temperatures during textile processing. Our bacterial cellulase is not eaten by protease, a protein that may be added to detergents.

"The bottom line is that replacing acid cellulase with bacterial cellulase should save money. And stones are not needed with the ORNL enzyme to stone wash jeans!"

Dees says the bacterial enzyme has been tested also on the wood chips used for bedding in ORNL's Mouse House, which shelters 300,000 mice. The bedding is replaced every few days, and the old chips are discarded. About 12% of the trash in the Oak Ridge Reservation's landfill consists of mouse bedding.

"After immersing mouse bedding in a solution of engineered enzyme," Dees says, "we reduced its volume and weight by 50% in 8 days."

Tim Scott, head of ORNL's Bioprocessing Research and Development Center in the Chemical Technology Division, has immobilized the genetically altered bacteria on beads in a fluidized bioreactor. His experiments have shown that these bacteria effectively convert cellulose to wood sugar. Other bacteria can be used to turn this sugar into alcohols, including the liquid fuel ethanol that can be used to power automobiles.

The bacterium has also been shown to grow in high concentrations in a solution of compounds that are toxic to many bacteria, such as saccharinic acid, furfural, and cinnimyl alcohol. Thus, the bacterium and its enhanced enzyme will be useful in modifying industrial waste streams that contain cellulose, such as those from paper production.

—Carolyn Krause.

Bird Reproduction Unaffected by Moderately Contaminated Food Fish

Can birds that eat contaminated fish have as many young as birds that eat untainted fish? Since the 1960s, studies have shown that high levels of some environmental contaminants can adversely affect the health and reproduction of wildlife. However, according to a recently released study by ORNL, moderate levels of contamination have no apparent effect on reproduction in fish-eating birds.

Dick Halbrook, Glenn Suter, and Bradley Sample, scientists in ORNL's Environmental Sciences Division, have found no apparent difference in reproductive success between great blue heron or osprey that eat moderately contaminated fish and birds of the same species that feed on uncontaminated fish. However, in a related experiment they found that a mammal species, the mink, had fewer young after eating fish from contaminated streams (fish make up one-half of the mink's diet).

The great blue heron is a long-necked, fish-eating wading bird with a long tapering bill, large wings, and soft plumage. The osprey is a large fish-eating hawk. The mink is a semiaquatic carnivorous mammal that resembles a weasel and has partially webbed feet, a short bushy tail, and a soft thick coat.

Fish in nearby Poplar Creek and the Clinch River, where the ORNL study was conducted, are contaminated with

Studies like the Oak Ridge investigation help test the validity of models for predicting contaminant effects on ecosystems.

polychlorinated biphenyls (PCBs), mercury, and other heavy metals. PCB and mercury levels in fish from the Clinch River and Poplar Creek are less than those seen in fish from locations in Lake Michigan. Contaminants in fish from the Great Lakes are suspected to have adverse effects on populations of fish-eating wildlife.

Halbrook reports that the eggs and chicks of the heron were found to contain PCBs and mercury, but their levels were less than those known to adversely affect other bird species. All heron chicks observed in this study were born normal and showed no defects. The number of offspring of the mink was lower than usual, but the young were normal.

For this study of ecological risk at a DOE site, Sample applied a pioneering ecological risk assessment method that Suter and Larry Barnthouse (formerly of ORNL) developed in the 1980s for the U.S. Environmental Protection Agency (EPA). EPA is currently using this method to assess the risk to the health of plants and animals of different types and levels of environmental contaminants.

The method considers several lines of evidence regarding the results and effects of contamination. Examples are the concentrations of each contaminant in the tissues of fish and of the birds eating them, damage to DNA in living cells and other bioindicators, reproductive success of birds and mammals exposed to contaminants, and the numbers and types of fish present.

Studies like the Oak Ridge investigation help test the validity of ecological risk assessment methods and models for predicting contaminant effects on plants, animals, and entire ecosystems.

A great blue heron in East Tennessee. Recent studies have shown that the reproductive success of great blue herons has not declined for those birds that eat moderately contaminated fish from Oak Ridge waterways. *Photograph by Ron McConathy.*

Such experimental results and field data allow risk assessors to correct their methods and models so that more accurate predictions can be made.

This project was conducted as part of the Comprehensive Environmental Response, Compensation, and Liability Act remedial investigation of the Clinch River and Poplar Creek and is being funded by DOE's Environmental Restoration Program. A primary objective of the remedial investigation was to determine whether contaminants pose a sufficient risk to human health or the environment to justify or necessitate cleanup actions.

—Carolyn Krause

Can Pond Sludge Be Mined for Useful Metals?

Studies of pond sludge from the DOE's Oak Ridge K-25 Site suggest there may be wealth in the waste. Tests by ORNL researchers show that, if the material is heated and cooled properly, a variety of minerals in the mud can be mined with a magnet. The remaining material is crushed glass, which could be inexpensively disposed of in a landfill.

Alex Gabbard and Charles Malone, both of the High Temperature Fuel Behavior Group in ORNL's Metals and Ceramics Division, conducted tests on surrogate sludge that contained a dozen nonradioactive metals and nonmetallic elements found in the actual sludge. These elements include aluminum, copper, iron, nickel, silicon, silver, sodium, and sulfur. The surrogate sludge did not contain uranium or other radioactive metals, which are present in the real material.

"Our experiments showed that cooking the pond sludge in graphite crucibles in an electrical resistance furnace has several effects," Gabbard says. "The volume of the material is reduced by more than two-thirds. The material is transformed into glass, or vitrified, in the shape of the crucible. And while a heated liquid, some valuable metals—mainly, iron, nickel, and copper—migrate to outer surfaces where they combine as 'gold spots' that can be easily separated magnetically from the rest of the material once it has hardened and is crushed. Recovering such useful metals is in the spirit of the Resource Conservation and Recovery Act."

Gabbard says the researchers have fully developed facilities to test actual pond sludge samples containing uranium or other waste materials (including those containing plutonium) to see if these elements also precipitate out of the mud as magnetic "gold spots" along with the iron, copper, and nickel. In Gabbard's vision, if this technique actually could mine uranium and plutonium from waste, the nuclear material extracted could be stored for potential use as fuel for nuclear power plants while solving a long-term waste problem.

When pond sludge from an Oak Ridge nuclear facility is heated in graphite crucibles in an electrical resistance furnace, glass globes covered with gold spots are formed. While the sludge is a heated liquid, some valuable metals—mainly iron, nickel, and copper—migrate to outer surfaces as gold spots. These metals can be easily separated magnetically from the rest of the material once it has hardened and is crushed.

The researchers do not yet understand why iron, nickel, copper, and sulfur in the sludge form golden globules that are not strongly attached to the rest of the material. Scanning electron micrographs show that the numerous iron-nickel-copper globules that make the black glass sparkle are surrounded by a sulfur skin. Gabbard thinks this skin may keep the spherical globules from bonding with the molten mud as it solidifies.

The formation and separation of the globules, Gabbard says, are likely due to the oxygen-free conditions created by the treatment method. To dry the sludge, an oxygen purifier was used to remove oxygen, and the sludge was heated to 1150°C in a nonoxidizing, helium atmosphere in the furnace. By contrast, in situ vitrification processes for turning radioactively contaminated soil into glass in tests at ORNL waste burial grounds add oxygen to the vitrified material.

The researchers also found that the best containers for the sludge were made of graphite, not ceramics. The ceramic crucibles became quite brittle and fractured during the heating process, but the graphite crucibles were not visibly affected and were reusable.

Pond sludge at the Oak Ridge K-25 Site is being stored in drums. DOE is evaluating a plan to dry the sludge, mix it with concrete, and repackage it in new stainless steel drums and overpacks. The packaged material would then be placed in storage facilities and indefinitely monitored. The cost of the project is estimated at from $90 million to $147 million.

Recovering useful metals is in the spirit of the Resource Conservation and Recovery Act.

The research was supported by the Environmental Management and Restoration Program led by J. M. Kennerly at the K-25 Site. The source of its funding is DOE's Office of Environmental Management.

While acknowledging the high cost of vitrifying the sludge by electrical resistance heating, Gabbard suggests that vitrification may be an economical approach in the long run.

"The metals in the mud are a resource that could be sold for industrial use," he says. "If uranium can be recovered by this technique, it could be sold for energy production. After the metals are separated out, the remaining crushed glassy material could be reclassified as a waste material that requires low-cost disposal.

This approach eliminates the need for long-term monitoring."

—*Carolyn Krause*

Computer Code Predicts Cancer Risk from Irradiation of Bone Marrow

A computer code for predicting the risk that a patient will develop cancer or die within 30 days of radiation treatment of bone marrow has been developed at ORNL. The code can be used to help plan a safe course of treatment for patients needing bone marrow transplants to boost or replace their immune systems or radiation therapy to kill cancerous cells.

Called MarCell (from marrow cell), the code was originally developed for the Department of Defense (DOD) and the North Atlantic Treaty Organization (NATO) to predict the survival rate for soldiers exposed to radiation for weeks or months during nuclear war. MarCell was developed by Troyce Jones, a researcher in ORNL's Health Sciences Research Division; Max Morris, a research statistician in the Computational Physics and Engineering Division; and Jafar Hasan, who spent an undergraduate science semester with Jones. Hasan, who was sponsored by DOE and ORNL under the Great Lakes Colleges Association/ Associated Colleges of the Midwest Oak Ridge Science Semester, was graduated recently from Albion College in Michigan. He has continued to work on the code as a consultant to ORNL.

"The development of the code led to a revolutionary finding about the nature of bone marrow," Jones says. "We found that the cells that were most radiosensitive, the stem cells, seem to be considerably less important than previously believed. We have found that the cells that are the most important—in fact, critical to the production of blood cells—are cells of the marrow stroma including fibroblasts.

"Fibroblasts and even stromal cells have traditionally been considered the least important cells in the complex process of blood formation. Our calculations support recent experimental evidence that stromal cells are critical to this process."

Besides DOD's Defense Nuclear Agency and the NATO applications, MarCell's capabilities are of considerable interest to the National Aeronautic and Space Administration (NASA). NASA's Langley Research Center in Hampton, Virginia, will be using MarCell to determine the risk to astronauts posed by radiation doses from solar flares and cosmic rays in outer space. Astronauts are exposed to space radiation during shuttle flights and work on orbiting space laboratories. NASA plans to use MarCell to determine shielding needs and formulate guidelines for altering or ending an individual's space activities.

"We think our code also can be helpful for doctors and patients planning bone marrow transplants," Jones says. "It can predict the risk of total body cancer and leukemia from various sources, levels, and dose rates of radiation from medical, occupational, and environmental exposures."

Recently, human data on leukemia and lymphoma cells have been used to model response kinetics of those malignant cells, as compared with normal stem and stromal cells. For the malignant cells, cell proliferation rates or cancer doubling time data can be entered for the individual patient.

Before receiving a bone marrow transplant, a patient must be given radiation and cytotoxic chemicals to suppress the normal immune response. Otherwise, the body would reject the transplanted marrow through a strong reaction known as graft-versus-host disease. Also, because leukemia originates in bone marrow cells, it may be necessary to kill the existing marrow and then transplant healthy marrow from a matched donor.

For aplastic anemia, a marrow transplant is needed to replace the "lazy" cells that fail to supply the needed blood cells. The lazy cells are destroyed by radiation and replaced by cells that proliferate more readily.

In radiation therapy for leukemia or aplastic anemia, for example, a patient may undergo several treatments spread out over a few days. A patient may receive a total dose of 1000 to 1200 rads of gamma radiation at less than 10 rads per minute. The radiation source may be cobalt-60, cesium-137, or more modern procedures such as proton therapy.

"The user-friendly code helps you decide how many radiation treatments are needed, how to minimize risk to the patient, and how long the recovery period will last for a particular course of treatment," Jones says. "It provides some information on patient responses to different therapeutic aids such as antibiotics and blood transfusions. MarCell models the rate of cell loss and recovery for marrow stromal cells and stem cells exposed to 12 types of radiation, including X rays, gamma rays, neutrons, beta radiation, tritium, and mixed fields of neutron-gamma radiations.

In response to menu selections, the user simply enters dose, dose rate, number of exposures, and time between each exposure. A graph appears that reveals how many bone marrow cells die and how fast during treatment. An option permits the same graph to show how different cell lineages repopulate during, between, and after individual radiation treatments; some of the injured marrow

The development of the code led to a revolutionary finding about the nature of bone marrow.

cells may proliferate and replace some of the normal bone marrow stem cells. MarCell calculates the increased risk of cancer of the blood and lymph glands that results from marrow transfusion or immunosuppression.

Since the 1970s, Jones had long been interested in modeling bone marrow kinetics, but the standard approach did not work adequately. Then he and Morris decided to work backwards by starting with data on survival and death rates of animals exposed to known doses of radiation that were delivered over the course of hours, days, and months.

"We used data on more than 18,000 test animals including mice, rats, dogs, sheep, swine, and burros," Jones says. "These experiments were conducted in the 1950s and '60s by the U.S. Atomic Energy Commission and British Medical Research Council. To estimate risk of cancer and leukemia, we used risk coefficients based on the response to radiation of radiologists, atomic bomb survivors, and victims of radiation accidents."

Early bone marrow codes that attempted to model cell losses and recovery and predict risk of death failed for marrow cells irradiated over a long time. "The approach," Jones says, "was to model long-term repopulating stem cells as the most radiosensitive and as the cells most critical to blood formation. The reason is that stem cells are the parents of specialized marrow cells, such as platelets (which stop bleeding), red blood cells (which carry oxygen), white blood cells (which fight disease), and malignant cells that cause leukemia and lymphomas.

"We tried a different approach," Jones says. "Morris used special techniques to estimate the numerical constants in our equations. The equations are based on simple models that show how marrow cells can be grouped into normal, injured, and killed cells and how new cells must be supplied to replace the killed cells."

Morris used a powerful workstation computer to run the math backwards from all the dose responses to optimize the numerical coefficients in the model. He related known radiation exposures to animal survival and death rates and to cell survival and death rates.

Hasan made the code more user friendly for the medical community. He also modeled malignant cell kinetics.

The ORNL scientists were the first to use modern statistical techniques and sophisticated computing power to address the thorny problem of the death rate and growth rate of irradiated bone marrow cells.

"Our big surprise was that the results of Morris's calculations did not describe stem cells as the cells most critical to the survival or death of an animal. I suggested that stroma cells might be more critical than believed, and the results on both animal and cell survival rates matched these theoretical cells of the mathematical model."

Jones said this finding has been confirmed by more recent experimental work. The evidence shows that stroma cells (stroma means "bed" in Greek) do much more than simply serve as a supportive layer to which stem cells must attach before they can proliferate. "These fatty yellow cells," Jones notes, "produce growth factors, or cytokines, that tell stem cells when and how fast to divide and how to differentiate into platelets and red, white, and other kinds of blood and lymphatic cells.

The ORNL scientists' code calculations led to 10 papers in a number of journals including the *International Journal on Radiation Oncology*. A drawing by ORNL graphic artist Allison Baldwin concerning their work graces the cover of the June 1993 issue of *Experimental Hematology*.

Ron Goans and other scientists at Oak Ridge Associated Universities (ORAU) are interested in using the same methods to model losses and recovery of irradiated lymphocyte cells. Such information can serve as an early biological indicator of the response of victims of radiation accidents as well as the responses of patients to a series of therapeutic treatments.

Robert Ricks of ORAU's Radiation Emergency Assistance Center/Training Site (REAC/TS) has collected a wealth of data from the former Soviet Union concerning human response to the Chernobyl reactor accident. MarCell is expected to be useful in analyzing and standardizing these data and other information on accidental and therapeutic exposures in the REAC/TS data base.

—*Carolyn Krause*

A Diamond Rotor for a Nickel Micromotor

You can easily cut out a cookie from dough with a cookie cutter. With a little more effort, you can cut out a puzzle piece from plywood with a jigsaw. But how do you cut out a rotor for a micromotor from a diamond—especially if it's as small as the period at the end of a sentence?

Scientists at ORNL have worked out a method for making diminutive diamond devices. They are now collaborating with researchers in Research Triangle Park, North Carolina, to develop a nickel

We hope to apply our method to produce unique diamond-based microsensors.

micromotor with a diamond rotor on a silicon substrate.

Perfection of the technique for producing diamond-based microelectromechanical systems (MEMS) could lead to diamond microsensors. These could be used where other materials could not—in corrosive liquids, in the bloodstream, and in high-radiation environments such as outer space.

The ORNL developers are John Hunn, formerly a postdoctoral scientist in ORNL's Solid State Division and now a postdoctoral scientist in the Metals and Ceramics Division; and Steve Withrow and C. W. (Woody) White, both of the Solid State Division.

"The micromotor has one moving part—a gear-shaped rotor which turns on a fixed axle," Hunn says. "In the current state-of-the-art micromotor, the rotor hub and axle erode quickly because of mechanical abrasion. We propose replacing these critical components with diamond."

Diamond is preferable to other materials because of its wear resistance and low friction. It is also mechanically stronger and more resistant to attack by corrosive chemicals..

To initiate manufacture of the diamond device, Hunn and his colleagues used ion implantation on a diamond sample at the Solid State Division. Using the 1.7-million-volt tandem accelerator at ORNL's Surface Modification and Characterization Research Center, Hunn bombarded a diamond sample with carbon ions at 4 million electron volts. The ions penetrated to 1 micron below the surface before inflicting damage, creating a graphite layer inside the crystal.

The ion-implanted sample was then sent to Kobe Electronic Materials Center in Research Triangle Park. The center used microwave chemical vapor deposition to lay down a 30-micron diamond film. As a result, 31 microns of diamond laid on top of the sacrificial graphite layer.

To cut out a diamond rotor from the film sample, Hunn plans to use an ultraviolet laser at Potomac Photonics, Maryland, or in ORNL's Chemical and Analytical Sciences Division.

The laser beam will cut a trench through the film down to the graphite layer, outlining the shape of the rotor, which will be 31 microns thick and 100 to 400 microns in diameter, or about the size of the period at the end of this sentence. The laser is stationary, but a computer-controlled table moves the sample under the vertical laser beam to cut the trench in the desired shape.

"You step the laser around the pattern some 20 to 30 times," Hunn says. "As the table moves, each pulse from the focused laser microbeam removes a spot about 10 microns in diameter and 1 micron deep. The spots overlay, forming a continuous trench."

The final step is to heat the sample in a Solid State Division furnace under flowing oxygen. The oxygen burns away the sacrificial graphite layer, etching under the laser-patterned diamond film. Graphite burns at a lower temperature than diamond because the bonds between the carbon atoms are weaker. When all the graphite has been removed, the diamond rotor is freed from the surrounding crystal and can be lifted out.

"I use the static electricity on a bit of plastic to manipulate the tiny diamond shape," Hunn says. "The 0.25-millimeter-thick, 3-millimeter-square diamond substrate can be reused to reduce production cost."

The nickel micromotors, whose rotors will be replaced with diamond, have been manufactured on 1 square centimeter of "real estate" purchased on a 6-inch silicon wafer. This multi-user MEMS

ORNL scientists have worked out a method for making a diamond rotor for a nickel micromotor on a silicon substrate. The diamond rotor would be about the size of the period at the end of this sentence. In this micrograph, a miniature, 13-micrometer-thick, single-crystal diamond star made at ORNL sits on top of a period on a piece of paper.

process (MUMPs), made available through the Microelectronics Center of North Carolina, allows researchers to obtain individualized MEMS processing at less than 1% of the cost for an entire wafer.

This research was supported by DOE's Division of Material Sciences, Basic Energy Sciences, and in part by an appointment to the Oak Ridge National Laboratory Postdoctoral Research Program administered by the Oak Ridge Institute for Science and Education.

"The hybrid diamond-nickel micromotor is an interesting example of this fabrication technique," Hunn says. "However, in order to find a market for diamond MEMS, one must invent a usable product that cannot be made from cheaper and easier-to-process materials. In the future, we hope to apply our method to produce unique diamond-based microsensors that would have real technological applications."

ORNL Inverter: Help for Electric Vehicles?

Electric cars and buses, adjustable-speed motors, heat pumps, fans, and compressors may benefit from a new electric power inverter developed by ORNL researchers. Inverters, used with many electric devices and motors, convert available power to the type needed—such as direct current to alternating current.

The Resonant Snubber Inverter (RSI), invented by engineers in the Digital and Power Electronics Group in ORNL's Engineering Technology Division, improves the efficiency and reliability of electric devices. In addition, it is smaller and lighter than other inverters, it greatly reduces electromagnetic interference (EMI), and it potentially lowers the cost of electric power inverters.

The RSI is about 80% efficient at low speeds and 98% efficient at high speeds. Conventional inverters lose more energy; they are about 60 to 70% percent efficient at low speeds and 94% efficient at high speeds. Inverter efficiency gains of that magnitude—especially at the lower speeds typical of its use in a car—could help electric vehicles become a viable option, researchers say.

To do their job, inverters employ a series of switches and electronic components. A conventional electric power inverter consists of six semiconductor power switches that turn on or off about 20,000 times per second in different combinations to provide the desired output. The inverter switch turns on and off at full voltage and current, generating a huge, wasteful power spike. This type of "hard switching" is an effective way of obtaining a specific current; however, this circuit design causes many problems.

The conventional inverter is noisy, big, heavy, unreliable, and expensive, says ORNL researcher Jason Lai, who works with ORNL co-inventors Bob Young, Matt Scudiere, John McKeever, George Ott, and Cliff White and University of Tennessee co-inventors Daoshen Chen and Fang Z. Peng. All are members of the Digital and Power Electronics Group, which is led by Don Adams.

In addition to EMI caused by hard switching, Lai says, conventional inverters put considerable stress on silicon devices and other parts within the inverter, causing reliability problems.

Although the conventional inverter uses six switches to achieve a desired output, the RSI adds three small auxiliary switches that temporarily—and very briefly—divert current, then route it back to one of the six main switches. This diversion, which lasts only a couple of microseconds, produces a zero voltage across the switch, helping reduce damaging power spikes. The RSI's "soft switching" increases efficiency from 4 to 15 percentage points over that of a conventional inverter. The efficiency gain

An ORNL-developed electric power inverter offers more efficiency and reliability and less electromagnetic interference than conventional power inverters. Bob Young (left) and Jason Lai are two of the inventors of the Resonant Snubber Inverter (RSI), which is smaller and lighter than conventional converters, like the 70-kw unit in the foreground. Young and Lai are holding a 100-kw RSI.

The ORNL device is being incorporated into an advanced air conditioner to be installed on electric buses.

depends on the speed of the motor connected to the inverter. Greatest efficiency gains occur when the motor is run at less than full speed, typical of an inverter's function in an electric vehicle.

An even more important advantage of the RSI is that it virtually eliminates EMI. Tests using an oscilloscope show EMI is greatly reduced compared with conventional hard-switching inverters and previously developed soft-switching inverters. EMI can interfere with the operations of appliances, telephones, electronic instruments, television reception, and other electronic equipment, such as computer-controlled ignition in automobiles.

Another benefit of the RSI is that it reduces voltage and current stress to inverter components. This feature improves the reliability and allows the use of lower-cost power devices. Because the RSI smoothly, or softly, changes the voltage and current during device switching, it can also help reduce the possibility of motor failure caused by insulation breakdown and bearing overheating. Soft switching also reduces the inverter's operating temperature, lessening the need for large, heavy heat sinks—devices to dissipate heat. Instead, the RSI can use smaller, lighter, and less expensive heat sinks to absorb excess heat before it degrades electronic equipment and causes failures.

The latest 100-kilowatt, three-phase RSI built by ORNL researchers is compact, measuring 9 by 12 by 6 inches and weighing 20 pounds. Hard-switching inverters from several years ago were bulky and weighed several hundred pounds. Even newer state-of-the-art inverters weigh two to three times as much as the RSI.

In addition to its use in electric vehicles, another likely application for the RSI is in heat pumps. According to McKeever, using the RSI and fans that run continuously, comfort levels and efficiency levels could be increased.

The research was supported by DOE's Laboratory Directed Research and Development fund.

In a different project led by Adams, an RSI is being incorporated into an advanced air conditioner to be installed on electric buses, including one in Chattanooga in 1997. The unit is the product of ORNL's work in advanced electric motor technology and work in developing a new air conditioner technology by a cooperative research and development agreement partner. Installation of the unit is expected to eliminate the need for an auxiliary power unit required for the bus's air conditioner. These auxiliary units are currently powered by propane, which results in emissions, noise, added weight, and increased cost. The RSI should make people more willing to leave the driving to the operator of the electric bus.

—*Ron Walli*

Mercury: Recent ORNL Advances

The following five highlights tell of recent achievements in ORNL's Environmental Sciences Division and Health Sciences Research Division in analysis of mercury in soil, water, and air and in removal of mercury from contaminated solid waste and soil.

ORNL Technique Measures Mercury in Water and Soil Fast

An economical, user-friendly technique for quickly measuring concentrations of mercury in water, soil, and sediment on site has been devised by scientists at ORNL. The technique, which can be easily learned and used by high school students, is expected to save millions of dollars if applied to remediation of mercury-contaminated sites.

Already the costs of developing the mercury analysis technique have been recovered through costs avoided. In this case, it was used to make rapid estimates on site for the project to remediate the mercury-contaminated floodplain of Lower East Fork Poplar Creek in Oak Ridge, saving the remediation project at least $40,000.

The federal government has decided to excavate soil from areas in the floodplain having mercury concentrations above 400 parts per million—the selected remedial goal option. According to this plan, in 1997 about 20,000 cubic yards of soil will be removed from two sites along the creek and taken to a permitted landfill at the Oak Ridge Y-12 Plant for disposal.

To refine the extent of mercury contamination on the floodplain, workers collect samples and measure the concentration of mercury in each sample. By determining where surface soil contains 400 or more parts per million of mercury, they can estimate the amount and location of soil that must be excavated. Preparations for disposing of the contaminated soil in the landfill can then be completed.

"We first prepared and processed up to 150 samples in about 3 days," says Ralph Turner, developer of the mercury analysis method and a researcher in ORNL's

Ralph Turner draws an air sample from the headspace of a sample bottle containing mercury-contaminated soil.

Environmental Sciences Division (ESD). "Technicians dried, pulverized, and digested the soil samples. It then takes about 20 minutes to do an analysis on a soil sample and 2 minutes to analyze a water sample using our technique. To date, we have processed nearly 1000 soil samples from the East Fork Poplar Creek floodplain."

Labor and material for one nationally recognized laboratory analysis technique cost about $90 a sample, but for ORNL's mercury analysis technique, they cost only $35 a sample. Based on these costs, Turner says, if the mercury analyzer were used to direct and confirm cleanup, the government would save several million dollars in floodplain remediation costs. The savings come from reduction in the cost of analysis and in the time that soil excavators and handlers are idle.

The ORNL mercury analysis technique should cut remediation costs.

DOE and the Environmental Protection Agency's (EPA's) Region IV have approved use of this technique for analyzing mercury levels in the East Fork Poplar Creek floodplain before remediation begins. "Our technique is likely to be used to confirm that cleanup of the East Fork Poplar Creek floodplain has achieved allowable levels," Turner says, " EPA has indicated likely approval of the technique for this activity."

Turner uses a commercially available, battery-powered mercury analyzer to measure the mercury vapor in the headspace (air at top) of the plastic bottle. Results of this measurement are used to calculate the concentration of mercury in the soil sample.

Mercury concentrations in floodplain soil must be monitored to ensure that all soil with mercury concentrations above 400 parts per million has been identified and to determine whether the remediation has been effective in meeting the remedial goal.

In the ORNL technique, the mercury-containing soil samples are chemically treated before analysis to transform the mercury into an easily detectable form. To liberate the mercury from the soil particles, the soil sample is digested using aqua regia—a mixture of hydrochloric and nitric acids used for dissolving platinum and gold. Because of the potential hazard of the mixture, the chemicals are mixed just before use. The ORNL group has conducted research on improving the safety of the technique by replacing aqua regia with an iodine-based extractant or by using a commercially available soil digestion kit.

For both water and soil samples, stannous chloride is added to convert mercurous mercury or mercuric mercury from the oxidized state (the state in which mercury lacks one or two electrons, making it a positively charged ion) to the most reduced state—elemental mercury. The tin in stannous chloride, which has been used for many years in conventional analyses, supplies the electrons to reduce oxidized mercury to the metallic element, which tends to escape from water to the air as a vapor.

The 1-liter plastic bottle containing the sample is then shaken by hand, causing about one-third of the elemental mercury in the soil solution to leave it as a vapor and to mix with air in the headspace—the space between the top of the solution and the container cap. "This partitioning of the volatile elemental mercury between a liquid and a gas according to Henry's Law is important," Turner says, "because the analyzer detects and measures only mercury vapor in air or some other gas, not mercury in water."

The amount of mercury vapor in the headspace is measured using a commercially available analyzer. The analyzer takes advantage of mercury's affinity for gold; the electrical conductivity of a gold foil in the analyzer is affected by the amount of mercury attracted to it, so the measured change in conductivity indicates the mercury concentration.

The battery-powered mercury analyzer is about the size of a big loaf of bread. Other materials used with it can easily be packed in a shoebox, except for the bottle in which the headspace measurements are made.

Turner conceived of the mercury technique when he was working with ESD's Steve Lindberg on a project funded by the Electric Power Research Institute. The two scientists were focusing on the exchange of mercury between air and water surfaces.

"That got me thinking about how one might apply Henry's Law in a field analysis of headspace vapor," Turner says. "Headspace analysis for volatile organic compounds, even in the field, is pretty well developed, but no one seemed to be doing mercury. I was also acutely aware of the need for a faster way to get mercury concentrations in the field and laboratory for water and especially soils. So I began developing the mercury technique using an old analyzer we had in the lab.

"While doing some private consulting to help study a problem with mercury in groundwater, I was asked how they might be able to rapidly map a mercury plume. I tried running some of the groundwater in their lab after adding a little bit of stannous chloride. I was amazed at the ability of the mercury analyzer to detect even a tiny bit of elemental mercury released from the groundwater. I convinced the consulting company to rent one of these conventional analyzers, which are widely available, and buy a bottle of stannous chloride. This earliest application worked very crudely, but it showed the potential."

Turner then asked the Environmental Restoration Division of DOE's Oak Ridge Operations to support further

I was amazed at the ability of the mercury analyzer to detect even a tiny bit of elemental mercury released from the groundwater.

development of the technique for analyzing both water and soil for mercury on the Oak Ridge Reservation. For this project, he hired Amanda Kriger, a chemistry intern from Oak Ridge Institute for Science Education.

"Amanda greatly refined the basic technique for water and developed a prototype technique for soil," Turner says. "After she left, I further refined the technique for analyzing soil. This refined technique is the one we now use daily.

"I also hired Norma Ayala, a postdoctoral chemist, to explore the iodine-based extractant approach. General Electric researchers had already shown that the extractant could be used to clean mercury-contaminated soil. GE gave us permission to explore its application in concert with our headspace analysis. Use of the iodine-based extractant proved more difficult than we thought because we could not use stannous chloride as the reducing chemical.

"My GE colleague Don Foust had suggested an alternative to stannous chloride: a common sugar called glucose. This actually works very nicely, but the whole procedure is still a bit more tedious and time consuming than the aqua regia–stannous chloride technique. I doubt this procedure will be widely adopted unless it can be streamlined."

Turner says that the ORNL field technique is at least as accurate as laboratory-type techniques. Our technique," he adds, "has probably had more performance testing in the real world and is probably a little less expensive than competitive field techniques. Also, the analyzer we employ in our technique can be rented widely."

The advantages of the mercury analyzer, Turner says, are that it can be used for rapid quantitative detection of mercury in water at industrial facilities; for rapid mapping of mercury contamination in soil, sediments, and groundwater in the field; and for rapid direction of soil cleanup activities and verification that the soil removed has unacceptable mercury levels and that the soil remaining is clean. "With our technique, there's no need to wait for lab results," Turner says, noting that the ORNL method "has revolutionized my own lab and field research activities involving mercury because each new idea can be quickly tested to see if it should be accepted or rejected."

The development of the mercury analysis technique was supported by the Environmental Restoration Division of DOE's Oak Ridge Operations.

Measuring Species of Water-soluble Mercury Gas in Air

Mercury is a heavy liquid metal, but it can float through the air as a gas. Researchers at ORNL have identified an important species of gaseous mercury in air that is highly soluble in water. This finding may help explain the concentration of mercury in precipitation and, as a result, in fish in lakes far from industrial discharges of mercury.

The discovery of a form of mercury in water was made by Steve Lindberg, a geochemist in ORNL's Environmental Sciences Division, and Wilmer J. Stratton, professor of chemistry at Earlham College in Richmond, Indiana, who conducted research at ORNL. Professor Stratton was visiting ORNL as the faculty director of the Oak Ridge Science Semester for students from the Great Lakes College Association.

"During dry weather," Lindberg notes, "this form of mercury would also be rapidly deposited to vegetation where it may be washed into soils and nearby streams."

They developed a novel technique using a type of cloud chamber, called a "high-flow refluxing mist chamber," to identify and measure reactive gaseous mercury, called Hg(II), in air. This type of mercury differs from elemental mercury, or Hg(0), which also exists as a vapor in air but is only sparingly soluble in water, in that the Hg(II) atom is missing two electrons. The actual compound in which Hg(II) resides is unknown, but Lindberg says it is most likely mercuric chloride.

Lindberg and Stratton's measurements indicate that 2 to 4% of total gaseous mercury in air is the highly water-soluble species and about 97% is elemental mercury vapor. "Because this low fraction is highly soluble in water," Lindberg says, "it is important to explaining the observed concentration of mercury in rain and snow, as well as the high rates of mercury dry deposition measured in some areas. Rain and dry deposition are important mechanisms for depositing atmospheric mercury on the earth's surface, helping to account for the high levels of mercury in the tissue of fish in lakes remote from man-made mercury sources."

The results should be of current interest because copies of a draft of an Environmental Protection Agency (EPA) report are now in the hands of members of the U.S. Congress. The EPA's Mercury Study Report, which is required by the Clean Air Act Amendments, noted the lack of data on airborne water-soluble mercury. EPA models indicate that a slight difference in the amount of mercury dissolved in airborne vapor could have a large effect on the amount of mercury deposited on the earth's surface.

Researchers at ORNL have identified an important species of gaseous mercury in air that is highly soluble in water.

Sources of Hg(II) emitted directly to the air are the burning of municipal and medical waste in incinerators and coal combustion. Although some coal-fired power plants have scrubbers to remove pollutants from flue gases, Lindberg says their removal efficiency for mercury varies from about 30 to 70%.

Lindberg first learned about the mist chamber when he met one of its developers in 1985 during a global climate change field study in a Brazilian rain forest. He was Bob Talbot of the University of New Hampshire.

Then, in 1990, while participating on a panel to review Sweden's mercury program, Lindberg first heard speculation about whether water-soluble mercury vapor may exist in the atmosphere because it had been identified in laboratory studies. He saw an opportunity to determine whether this species exists in outside air by a novel application of the mist chamber.

In 1993 Lindberg contacted Talbot and persuaded him to send ORNL a mist chamber. Lindberg and Stratton then found they could trap water-soluble Hg(II) in an aerosol mist in the chamber. With support from the Electric Power Research Institute, they conducted a number of tests at Walker Branch

Watershed near ORNL and near the Earlham College campus to verify that this species did not come from other sources such as oxidation of Hg(0) by ozone in the chamber.

"Swedish scientists had identified a water-soluble species of mercury in laboratory flue gases from coal combustion," Lindberg says. "But the director of the Swedish mercury program didn't think this species existed in outside air. It occurred to me that, if water-soluble mercury is in the air, it will dominate atmospheric deposition of mercury."

The finding is significant, Lindberg says, because the accuracy of predictions of computer models on atmospheric mercury transport and deposition depends largely on assumptions about the fraction of highly water-soluble mercury present.

"About 30 to 80% of mercury emitted to the air by combustion processes is in water-soluble form based on recent studies by Frontier Geosciences in Seattle, which is now collaborating with ORNL to test the mist chamber method," Lindberg says. "This Hg(II) is either deposited quickly or rapidly reduced to elemental mercury by sulfur dioxide dissolved in water. Elemental mercury is also dissolved in water, but Hg(II) is much more soluble in water and deposits much more rapidly."

Lindberg says the data suggest a link between rain and the atmospheric deposition of mercury in lakes far from industrial sources of mercury. The mercury is then transformed into methylmercury by bacteria. This compound, which is toxic to humans if consumed in even tiny amounts, is readily taken up by fish in these remote lakes.

Some geologists, however, argue that rock weathering, rather than atmospheric deposition, could be the chief source of mercury to these lakes. It is still not resolved whether mercury in waterways comes mainly from natural sources or from human activities such as waste incineration and coal combustion for electrical power production.

In the ORNL technique, a vacuum pump draws air through the mist chamber

Using a high-flow refluxing mist chamber such as this one at the Laboratory, ORNL researchers were the first to identify and measure reactive gaseous mercury in air.

from an inlet at the bottom. A mist is sprayed into the chamber. As the air passes through to the top, the highly soluble mercury in the air is dissolved in the mist. In the laboratory, the mercury is then reduced to elemental mercury with tin chloride (which adds the two missing electrons), stripped from the water droplets by purging with nitrogen onto a gold trap (mercury is attracted to gold). After the gold surface is heated to remove mercury, the concentration of mercury is measured by atomic fluorescence spectroscopy.

The ORNL discovery of highly water-soluble mercury in the background atmosphere was made in 1993, reported in 1994 at a scientific meeting, and published in 1995.

Lindberg, who is co-chairman of the conference entitled "Mercury as a Global Pollutant" planned for 1996 in Hamburg, Germany, and the developer of a U.S. network for monitoring the movement of toxic substances in the air, says: "Mercury is a very mobile metal because it exists so often in gaseous forms. It behaves less like a trace metal and more like some pesticides, PCBs, and other persistent organic pollutants. Because its various forms are volatile, it plays hopscotch—depositing on land and water from air, staying there awhile, and then reentering the air as a gas. In this way, mercury can be rapidly and widely distributed throughout the global atmosphere."

Green Plants Emit Mercury, ORNL Discovers

In the 1970s, researchers at ORNL discovered that green plants can take up mercury from the soil and from the air. Now, ORNL researchers have scientific proof that plants can also emit mercury to the air.

Paul Hanson of ORNL's Environmental Sciences Division (ESD) discovered that green plants can give off mercury during his study of mercury uptake in plants from air and soil. The study was conducted for the Electric Power Research Institute, the research arm of the electric utility industry. The goal of the study designed by Steve Lindberg of ESD and Hanson was to determine if the landscape is primarily a source of or sink for mercury—that is, whether it mainly emits mercury to the air or stores mercury deposited on it from air.

The project used two independent methods to measure the mercury fluxes, one in the laboratory and one in the field. To conduct the study, Lindberg and Hanson used a technique pioneered by Lindberg and Ki Kim, a postdoctoral scientist in his laboratory. This high-precision sampling technique measures the exchange of mercury between air and land.

"In the field, we measure mercury concentrations at various heights above the ground to get a concentration profile," Lindberg says. "If the mercury concentrations are higher close to the surface than farther above it, then the surface is a mercury source. If the reverse is true, more mercury is being deposited than emitted. These fluxes are mapped over various areas, and the data are used to answer such questions as whether the surface is primarily a source of or sink for mercury."

In his laboratory experiments, Hanson studied maple, oak, and spruce saplings in a chamber into which mercury-free air was introduced. Hanson developed the mercury chamber method using equipment developed for ground-level ozone studies in the 1980s at ESD. The soil the saplings were planted in was isolated from the chamber. Hanson sampled the air for mercury vapor. "To my surprise," he says, "mercury was coming from the plants!"

Further experiments showed that the plants take mercury from the air when the air's mercury level is above about 20 nanograms per cubic meter. When the mercury level in air is only 2 nanograms per cubic meter, the plants emit mercury. These levels of mercury are common near pollution sources and at background sites, respectively.

To my surprise, the tower data indicated significant emission of mercury from oak, hickory, and maple trees.

"Our theory," Hanson says, "is that elemental mercury in soil gas is pulled into the plant when the plant's mercury level is low. The plant tries to achieve equilibrium with respect to mercury levels in the air. When the plant's mercury level rises and the air mercury level decreases, at some point the plant releases some of its mercury by transpiration—the process of giving off vapor containing waste products through the stomata of plant tissues."

While Hanson was performing his studies, Lindberg, Kim, and Jim Owens of ESD climbed the 44-meter meteorological tower at Walker Branch Watershed near ORNL to measure gradients in mercury concentrations over the forest.

"To my surprise," Lindberg says, "the tower data also indicated significant emission of mercury from the oak, hickory, and maple trees below."

Lindberg also studied trees at a Christmas tree farm in Wartburg, Tennessee. These trees are too far away from Oak Ridge to be exposed to any mercury emissions there. He measured mercury concentrations in air, soils, *We also observed that the trees are a strong source of mercury to the air when they are dry.*

water, and vegetation at the Wartburg farm.

"We found that mercury deposits from the air to the trees when they are wet," he says. "But we also observed that the trees are a strong source of mercury to the air when they are dry, supporting the data from the ORNL studies."

In ORNL studies in the 1970s of mercury-rich soils near a large mercury mine in Spain, Lindberg, Danny Jackson, and John Huckabee found that these soils emit mercury vapors at a rate that depends on temperature and vegetation cover. "We found that crops grown on these soils accumulate mercury in two ways," Lindberg says. "The roots take up mercury from the soil, and the leaves absorb mercury vapor from the air. These pathways may provide important exposure mechanisms if humans consume either leafy or root-type vegetables grown on these soils."

ORNL's pioneering method to measure fluxes of mercury over the landscape has also resulted in another discovery. Anthony Carpi, a graduate student from Cornell University working in Lindberg's laboratory, found large gaseous fluxes of elemental mercury from sewage sludge applied to forest and farm soils.

"Sewage sludge used to fertilize soil is a previously unmeasured source of elemental mercury to the air," Lindberg says. "Carpi found that more mercury comes off agricultural soil than forest soil to which the same amount of sewage sludge is applied. The emission rates measured over sludge-amended soils exceeded those measured over forest soils at Walker Branch Watershed by a factor of 100 or more. He also discovered and measured emissions of methylmercury from sewage sludge."

This is significant because sewage sludge applied to soil is the only known terrestrial source of methylmercury to the atmosphere. Methylmercury is a highly toxic compound formed in the environment that can be a health hazard for humans when taken in as food.

In the ORNL studies, mercury vapor is collected in quartz glass tubes that contain acid-washed sand coated with metallic gold. When air is drawn through tubes at a prescribed flow rate, mercury vapor adheres to the gold. By heating the gold, researchers can measure the amount of mercury vapor released at a precision level of a few trillionths of a gram.

Process Removes Mercury from Mixed Waste

Some mixed waste on DOE's Oak Ridge Reservation contains mercury as well as other hazardous metals, toxic chemicals, and low-level radioactive substances. Can this mercury be removed to simplify and lower the cost of treating and disposing of the remaining waste?

Researchers at ORNL have shown that a commercially developed mercury-removal process they modified can extract mercury from mixed waste. In laboratory studies, the process has been shown to remove 99.6% of the mercury present in actual mixed waste and from synthetic soils, surrogate sediments, and crushed glass from fluorescent light bulbs.

In laboratory studies, researchers with the General Electric (GE) Company have shown that GE's patented potassium iodide–iodine (KI/I_2) leaching process can remove mercury from mercury-contaminated waste at elevated temperatures. Two ORNL researchers have shown that the process can work effectively on mixed waste at room temperature, and they have made other changes so that the leaching solution can be prepared more rapidly for recycling.

The researchers are Dianne Gates of the Environmental Engineering Group in ORNL's Environmental Sciences Division, and Thomas Klasson of the Remediation Technology Group in the Chemical Technology Division. In their tests, they use familiar objects such as glass flasks and steel wool.

"The mercury removal step is especially needed as a pretreatment for mixed wastes in which mercury is the chief nonradioactive material," Klasson says. "For example, mixed waste can contain mercury and low-level radioactive metals such as uranium, technetium, cesium, and strontium.

"It is desirable to remove mercury because it is volatile—it turns from a liquid metal into a gas," he continues. "If it's removed, the remaining radioactive waste can be treated with thermal processes that melt the components into a ceramic or turn them into glass.

"The design of the thermal treatment device would be simpler and less costly if volatile mercury is removed first. We would then have fewer gases to deal with during the heating process."

At nuclear facilities, there is also interest in removing mercury from burned-out fluorescent lights that are being stored as "administratively radioactive" waste because of the presence of radiation in the lights' original location. If mercury can be removed from this waste, which is stored as crushed glass, then the glass can be reused rather than stored as a waste. For example, it could be a starting material

Dianne Gates holds a flask of surrogate sediment to which mercury has been added. Thomas Klasson examines a flask containing a mixture of the mercury-contaminated sediment and the potassium iodide–iodine leaching solution. This flask will be placed in the environmental shaking chamber, which mechanically mixes the liquid and solid to separate out as much mercury as possible.

The design of the thermal treatment device would be simpler and less costly if volatile mercury is removed from mixed waste first.

for vitrification, a method for electrically heating radioactive waste to form a glass that traps the radioactive material.

"For actual mixed waste, we will not know what form the mercury is in," Gates says. "That's why we like this process. It attacks and isolates mercury in the elemental form and in any compound whether it be mercuric chloride or mercuric sulfide or mercuric oxide."

The iodine atoms in potassium iodide surround mercury atoms in any chemical form. Because of the strong attraction between both types of atoms, charged molecules called mercury iodide complexes form, trapping the mercury atoms in the leaching solution. Iodine in

We can separate mercury from the leaching solution using steel wool.

the leaching solution is used to oxidize elemental mercury (so it won't escape into the air as a vapor) and to attack mercuric sulfide, freeing the mercury ions from the sulfur ions.

In the ORNL experiments, 10 to 100 grams of mixed waste are poured into a 200-milliliter flask. The flask is placed in an environmental shaking chamber, which rotates and shakes for four hours to mix the solid waste with the leaching solution. Such mechanical mixing is required to maximize the contact between liquid and solid to separate out as much mercury as possible.

The next series of steps aims at removing the mercury from the leaching solution and replacing the solution's lost iodine, thus making it reusable for treating mercury-contaminated mixed waste. The solution must be recharged with iodine because some iodine is used up in oxidation. The mercury-bearing leaching solution is run through a column containing steel wool. The mercury forms an amalgam with iron in the steel wool.

"GE mixes the leaching solution with iron filings at elevated temperatures to remove mercury from the leaching solution," Gates says, "but we found that steel wool works better. We can separate mercury from the leaching solution using steel wool at room temperature in just one hour. Because the steel wool can be packed in a column, we have eliminated one separation step from the GE process. Then we use lime to remove any metals remaining in the solution and to convert all remaining iodine to iodide, in a procedure that takes 30 minutes. Finally, in approximately 1 hour we regenerate the required amount of iodine in the leaching solution by adding an acid and hydrogen peroxide. Altogether, the mixing, leaching, mercury separation, and regeneration processes take less than 8 hours." All in a day's work.

The laboratory-scale research was supported by DOE's Environmental Management Program, Office of Technology Development, Mixed Waste Integrated Programs. The ORNL researchers are seeking funding to test the pretreatment technology at an engineering scale inside a building.

ORNL Method Removes Mercury from Soil

The Oak Ridge Reservation has soils that are contaminated with mercury because of human activities. That's the bad news. The good news is that the reservation also is blessed with microbial organisms that could be the key to releasing its soil mercury. Here's the story.

About five years ago, Richard Tyndall, then of ORNL's Health Sciences Research Division, discovered a consortium of bacteria that resides within amoebae in soils on the Oak Ridge Reservation. These one-celled organisms apparently serve as a protective niche for the bacteria. Arpad Vass of the same division isolated bacteria from the amoebae and found that the bacteria produce a powerful biodispersant that breaks up oil. It was thought that these isolates could be used to break up slicks from the 1989 Exxon Valdez oil spill into Prince William Sound that was environmentally damaging to Alaskan birds and fish. However, the idea was never tried.

"As we continued to experiment with this isolate," Vass says, "we found that it can break clumps of soil into fine, dustlike particles, just as a detergent separates grease particles. After more experimentation, we found that it could emulsify mercury—something that was unheard of."

Vass and Tyndall discovered that the bacterial isolate could produce a suspension of tiny globules of mercury in a liquid consisting of water and soil fines. However, as in an emulsion of oil in vinegar, the globules of mercury will not mix with the soil fines in the liquid. Says Vass, "We believe that the biodispersant overcomes the attractive forces between the soil particles and the mercury, thus allowing the mercury to separate from the soil."

Tyndall and Vass then contacted their supervisor Clay Easterly to let him know what they were trying to do. "I told him I was interested in finding a practical method to remove mercury from soil, because I had heard about the mercury contamination of soil around the Oak Ridge Y-12 Plant," Vass says. "My idea was that, since the biodispersant not only breaks up soil fines but also emulsifies mercury into thousands of small beads, we could use electroplating to remove mercury from the soil. This scheme didn't work, so we called Clay and he suggested that we use copper."

Easterly recalled to them his days in high school chemistry class when students used mercury to shine copper pennies, giving them the luster of dimes. "People used to coat nearly worthless copper coins with mercury to make them look like valuable silver coins," Easterly told Vass.

"So we tried many different copper sources, but most had improper surface conditions to amalgamate efficiently with the mercury," Vass says. "We went back to Clay and he said, 'Try pennies.' His idea worked. The mercury was attracted to the copper. Then I suggested using a magnet to remove the two metals. Clay

Our process can remove elemental mercury more efficiently than any other process we know about.

came up with the idea of penny surrogates—BBs with iron cores and a copper coating."

The new ORNL biodispersant-based amalgam process uses an intra-amoebic bacterial biodispersant to break up the soil in a rotating cylinder and copper-coated iron pellets to attract the mercury. The mercury-covered pellets are extracted with a magnet. They are then placed in a vacuum oven where the heat separates the mercury from the copper.

"Our process can remove elemental mercury more efficiently than any other process we know about, and it will save time and money," says Easterly. "It will also eliminate the costly prospect of permanently storing thousands of drums containing mercury-contaminated soil in controlled hazardous waste sites. We are moving away from a system that stores mercury-contaminated soil to one that cleans it up. This new method allows us to remove a heavy metal that can pose a health risk in certain chemical forms and to return the soil to the land to be used again."

"The key to this process is the biodispersant, which is naturally occurring, nontoxic, and biodegradable," Vass says.

The problem with the process, Easterly says, is that the soft copper on the BBs rubs off. He hopes that ORNL's Metals and Ceramics Division can develop a hard magnetic copper alloy and that the material can be formed with dimples like a golf ball to present more surface area for attracting mercury.

The ORNL biodispersant-enhanced amalgam process can be used to remove elemental mercury from soil, such as that at the Y-12 Plant and other industrial sites. Because the process is an amalgamation, it would not remove mercury compounds like mercuric sulfide. Mercuric sulfide formed in the soil of the floodplain of East Fork Poplar Creek in Oak Ridge after the creek received releases of mercury from the Oak Ridge Y-12 Plant in the late 1950s and early 1960s. Mercuric sulfide, which is very insoluble, is not readily taken up by the body; elemental mercury is more hazardous to human health.

The biodispersant obtained from the bacterial isolate, which could be used in this process, will be particularly helpful in extracting mercury from contaminated areas on the Oak Ridge Reservation that have what Easterly calls "very tight soils." Tight soils make it more difficult to break the soil into smaller pieces for better contact between the copper and mercury.

No dangerous chemicals are used in the removal process. Both the cleansed soil and the copper pellets can be used again. The reclaimed mercury can be sold to industries that need the element for their manufacturing. Other advantages are the mobility of the equipment, short setup time, and minimal environmental hazard during the operation.

"Sale of the mercury could offset the cost of processing, particularly when you consider the costs of the alternative of storage or disposal of the contaminated soils as hazardous waste," Easterly says. The cost of the low-technology equipment is anticipated to be less than storage of mercury-contaminated soil or any other methods involving chemistry or high energy use (such as incinerating the soil).

The new mercury-removal process helps to fulfill an ORNL mission of finding more efficient, less costly ways to clean the environment to comply with the law and protect human health. Fortunately, some home-grown technologies may help us solve some problems at home. —*Carolyn Krause*

Linking Tennessee Students to a World of Information

Tennessee students can travel the world on their fingertips while never leaving the room using Internet programs supported by DOE and managed by ORNL.

Through the Oak Ridge Educational Network (OREN) and the Adventures in Supercomputing (AiS) programs, DOE and ORNL have helped open computer windows in 59 Tennessee schools to a world of learning on the Internet. These programs help students search the world in a few seconds to answer seemingly unsolvable questions, such as tricky calculus problems. From kindergartners to seniors in high school, students can easily discuss politics with students and professionals in other countries, approximate the potential crop growth in Tennessee, or pinpoint the year in which Benjamin Franklin discovered electricity.

In rural settings, students have a hard time getting the type and amount of information that is available on the Internet, says David Staten, who teaches computing and math at Wartburg Central High School, which has about 450 students in grades 9 through 12. "Students in rural areas like Wartburg don't have access to extensive research libraries like those at the University of Tennessee, where hundreds of resources are kept current," he says. "However, with the Internet they can now go around the world without leaving the classroom."

Since Wartburg Central students have had access to the Internet, their interest in computers has increased and the school's computer class has tripled in size, Staten said. Wartburg Central

In rural settings, students have a hard time getting information.

Students at Central High School in Wartburg, Tennessee, have access to a world of information through the DOE-funded Oak Ridge Educational Network and the Adventures in Supercomputing programs. Left row, from front: Casey Will, Heidi Obidzinski, Matthew Yu; right row, from front: Billy Brasel, Jamie Jones, and David Staten (teacher). *Photograph by Curtis Boles.*

Since Wartburg Central students have had access to the Internet, their interest in computers has increased.

High School draws students from one of the lowest per capita income areas in Tennessee. The high school was selected to participate in the AiS program, and DOE provided computers for the school.

The AiS program is aimed at cultivating the interests of minority, female, and economically disadvantaged high school students in mathematics, science, and computing. The program simulates scientific experiments, which are safer and less costly than doing experiments in a laboratory. AiS students use high-performance computers, graphic workstations, and networks to conduct experiments that can be too complex or dangerous to study in a laboratory. For example, students can easily perform simulated crash tests to understand crash dynamics without the costs of using real cars. Supercomputing can also help predict the spread of fire or the path of a tornado.

Unlike AiS, OREN is a wide area network that connects elementary, middle, and senior high schools in Oak Ridge and more than a dozen counties, primarily in East and Middle Tennessee, to Internet tools. These help students explore physics, chemistry, art, and many other subjects that they ordinarily would not be exposed to until high school. OREN provides all Internet services, including global electronic mail, network news services, World Factbook, weather maps, and many other resources in science, mathematics, social sciences, and humanities.

"The scientific world increasingly relies on Internet computer tools to do research, solve mathematical problems, and simulate and model science experiments," says ORNL Director Alvin Trivelpiece. "By linking schools to the Internet, ORNL can help students get excited about learning new ways to analyze scientific data or write computer programs. The Internet will revolutionize the way students work and think by helping them tap into resources from around the world."

Since October 1991, DOE and ORNL have invested $2.6 million in computers, software, training, and networks to provide the AiS and OREN to Tennessee school programs. Schools in 15 counties and two cities are connected to the Internet through hubs in Memphis, Nashville, Knoxville, and Oak Ridge. Participating Tennessee counties are Anderson, Campbell, Davidson, Gibson, Giles, Grundy, Knox, Lawerence, Madison, Monroe, Morgan, Murfreesboro, Rhea, Roane, and Union. Connected cities are Oak Ridge and Memphis. A dial-up modem pool can be provided so that students and teachers with home computers can connect after school hours.

For each AiS school, DOE and ORNL helped provide four Macintosh computers with color monitors and printers, training for teachers at a Summer Institute, experienced consultants to provide support, and high-performance computing with a parallel computer on loan from nCUBE Inc. At the 2-week Summer Institute, teachers receive hands-on training to guide students in programming solutions to scientific problems. At the end of the session, teachers get software applications and materials to take back to their respective schools.

"Getting Internet to our schools has been one of the most successful outreach programs to come from the Laboratory," says Dr. John Wooten, ORNL's program administrator for Educational Technology. "It is a crucial step in integrating and moving technology forward into the classroom."

OREN furnishes dial-up connections to at least 1200 Tennessee users. Through OREN, the Oak Ridge Regional Science Education Center was equipped with modern Sun Sparc-10 UNIX-based computer workstations and phone lines from ORNL for hands-on science experiments and full Internet access. At the Science Education Center, students can use modern telecomputing for science data collection and observation.

Through the OREN program, DOE and ORNL have helped to train more than 1000 teachers in computer technology. The program has also provided free, advanced computer training for more than 300 teachers and students at the Saturday Academy for Computing and Mathematics (SACAM). Here, ORNL volunteers teach students to use computing and mathematical tools to solve problems, such as determining sequences of DNA bases in the human genome—information that could lead to a cure of genetically linked diseases.

In addition to OREN, the AiS program has connected 15 high schools, or more than 3000 enrolled students, to supercomputing programs. This year, DOE and ORNL are trying to expand the program into junior high schools.

—April Davidson

Virtual Textbook Popular with Internet Users

***Editor's note:** Here is a condensed version of a newspaper column by Alvin Trivelpiece, ORNL director.*

URL: http://csep1.phy.ornl.gov/csep.html

Point your browser to this address on the fantastic information resource known as the Internet and you will call up ORNL's popular "textbook" that has never been printed by a book publisher. Our Computational Science Education Project (CSEP) has been seen by more than a quarter of a million people, but you can't find it at the local bookstore. CSEP is the first-ever "virtual textbook," which exists only in that electronic information medium we call Cyberspace. It is currently used at more than 20 universities.

This project was the brainchild of the DOE's Office of Energy Research, and the scientists and computer experts at ORNL took the lead role in creating CSEP. Its home is a computer in ORNL's Physics Division, but the usage has been so great that one computer can't handle the demand.

Ten "mirror" computers around the world now contain CSEP. This backup system exists at Vanderbilt University, Colorado State University, the University of Kentucky, Drexel University (Philadelphia), Tampere University of Technology (Finland), National University of Singapore, the University of Frankfurt (Germany), the University of Giessen (Germany), Universitat Tübingen (Germany), and Edinburgh University (United Kingdom).

A normal textbook limits your information search to only those words on the printed pages. However, our computer-based book allows you to travel to many other information resources with just the click of a mouse. You might start on that computer in the Physics Division at ORNL, see something that grabs your attention, and click into material residing in a computer at Oxford University or Yale. You might wonder how scientists in other disciplines are able to apply approaches you read about in CSEP, so this "virtual textbook" makes it possible for you to cross disciplines.

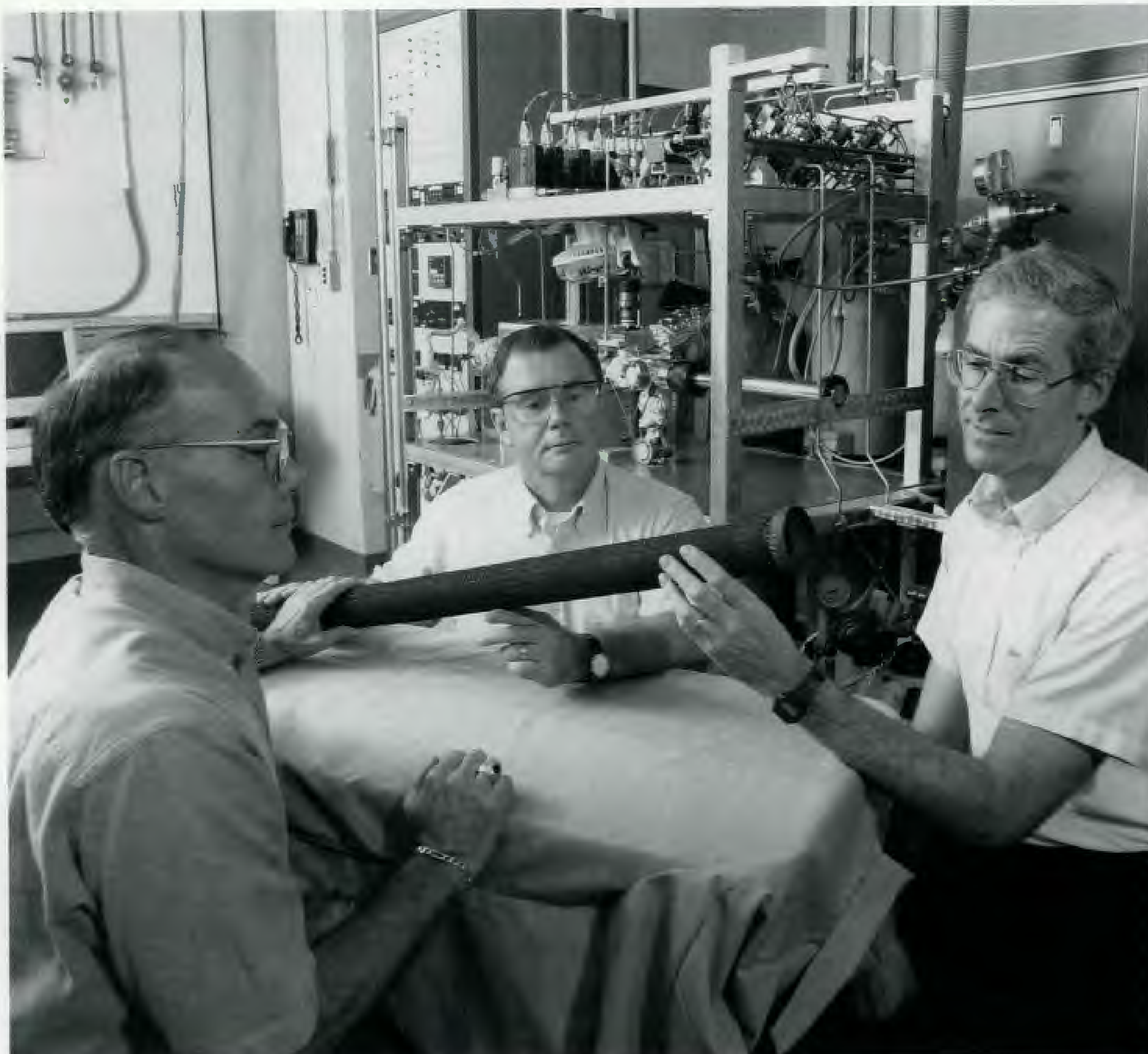
The long list of this textbook's authors includes such experts as the late Chris Bottcher and Michael R. Strayer of ORNL, Richard C. Allen of Sandia National Laboratories, Phillip Bording of the University of Tulsa, William Martin of the University of Michigan, and Geoffrey Parks of Cambridge University. Verena M. Umar of Vanderbilt University is editor for contributions to the book. Each article is reviewed by an expert before it is accepted.

Our Computational Science Education Project is the first-ever virtual textbook.

If your interest in computational science is narrow and if you're in a hurry, you can search the electronic textbook by keyword. Let's say you're interested in parallel computing. If you type "parallel computing" in the keyword search area, almost immediately you will be shown a list of more than 100 documents containing that term.

Nothing like CSEP had ever been done before. CSEP is, if not the best example, then certainly one of the best examples of how the Internet already is having a major impact on the dissemination of information. **ornl**

Ceramic Filter Is Key to Advanced Coal Technology



Developers at ORNL of the 3M ceramic composite filter for combined-cycle fossil fuel plants include, from left, Jerry McLaughlin, Rod Judkins, and David Stinton. Not pictured is Rick Lowden, another ORNL developer of the filter, which received an R&D 100 award for 3M and ORNL in 1995.

The road to technology transfer has its twists and turns. The design of the commercially available 3M ceramic composite filter, which earned 3M and ORNL an R&D 100 Award in 1995, is a case in point. The story behind this development underscores the significance of networking to perceive market needs and of "people skills" to convince companies that needs for specific products exist. Also important is teamwork in the use of technical skills for developing products. Putting money in the right places also helps.

In 1984, David Stinton of ORNL's Metals and Ceramics Division was asked to develop a process to fabricate a special type of ceramic composite for DOE's Fossil Energy Materials Program. The project had a long-term goal: develop highly dense silicon carbide composite tubes that have high thermal conductivity so they can be used as heat exchangers. It was thought that such tubes would be needed in advanced combined-cycle fossil plants in 10 years or so.

So Stinton worked on developing a dense fiber-reinforced silicon carbide composite tube that would meet the long-term need. As he conducted his research, ORNL's fossil technology program managers, Ron Bradley and Rod Judkins, visited a number of experimental combined-cycle power plants—integrated coal gasification and pressurized-bed coal combustion combined cycles. These are facilities in which coal is burned to produce hot gases that drive a gas turbine as well as heat that makes steam to spin a steam turbine. This so-called combined cycle is expected to be 35 to 50% more efficient than today's coal-fired steam power plants. It is believed that, as natural gas becomes less abundant and more expensive, many combined-cycle fossil plants will be built to generate electricity.

During these visits in 1985 and 1986, Bradley and Judkins kept hearing about an immediate problem facing operators of combined-cycle fossil plants. The operators rarely mentioned heat exchangers. But they talked a great deal about the breakage of candle filters that remove coal ash from the hot gases produced in coal combustion or gasification. The ORNL managers also heard about the filter problem through their interactions with DOE's Morgantown Energy Technology Center (METC). METC was sponsoring a project at Westinghouse's Waltz Mill site, which had been experiencing filter problems at its coal gasification pilot plant.

I came up with the concept of changing the process to make tubes that are 60% dense—porous enough to serve as filters.

These filters are important because they prevent the ash from striking the blades of the gas turbine. "When the filters break," Stinton says, "ash particles get through and erode the metallic blades. Also, the blades can be corroded by chemicals in the ash."

The filters now in use are made of silicon carbide particulates bonded together by a glassy matrix consisting of aluminosilicate clay. These filters can break because of thermal shock—large and rapid changes in temperature—which occurs when the filters are cleaned during plant operation.

"The gas flows from the outside of the filter tube to the inside," Stinton says. "The ash particles in the gas cannot get through the filter material, so they are trapped as a cake on the outside of the tube. To clean the outside of the tube, air or gas inside the filter is blown repeatedly to the outside. Because the cleaning gas is colder than the gas being filtered, the filters undergo thermal shock."

In 1986, Judkins informed Stinton that the advanced combined-cycle plants have an immediate need for ceramic filters that don't break at temperatures as high as 850°C. Says Stinton: "I told him that the process for producing fiber-reinforced silicon carbide tubes that are 90% dense for heat exchangers could be modified to make tubes that are 60% dense—porous enough to serve as filters."

The filter tubes were made using chemical vapor infiltration and deposition of a ceramic matrix into a structural form (fibrous preform). Special gases are introduced to the preform, which is heated to cause silicon carbide to form and deposit uniformly throughout the preform.

Using a small amount of funding from DOE's Office of Fossil Energy Advanced Research and Technology Development Materials Program, Stinton explored the concept and found it promising. Subsequently, with funding obtained through METC, Stinton worked on the filter development with Judkins, Rick Lowden, Laura Riester, and Jerry McLaughlin, all of the Metals and Ceramics Division. He later talked to filter manufacturers to find out ways to improve the filter. One suggestion was to make its wall thinner so the filter is lighter and creates less pressure drop. The ORNL scientists found a way to do this.

"If lighter filters are used," Stinton says, "then the structures built to support hundreds of them, called tubesheets, would be simpler and cost less. Also, less cooling water would be needed for the tubesheets, which would save energy."

ORNL lacks the facilities to fabricate and test candle filters, which are each 1.5

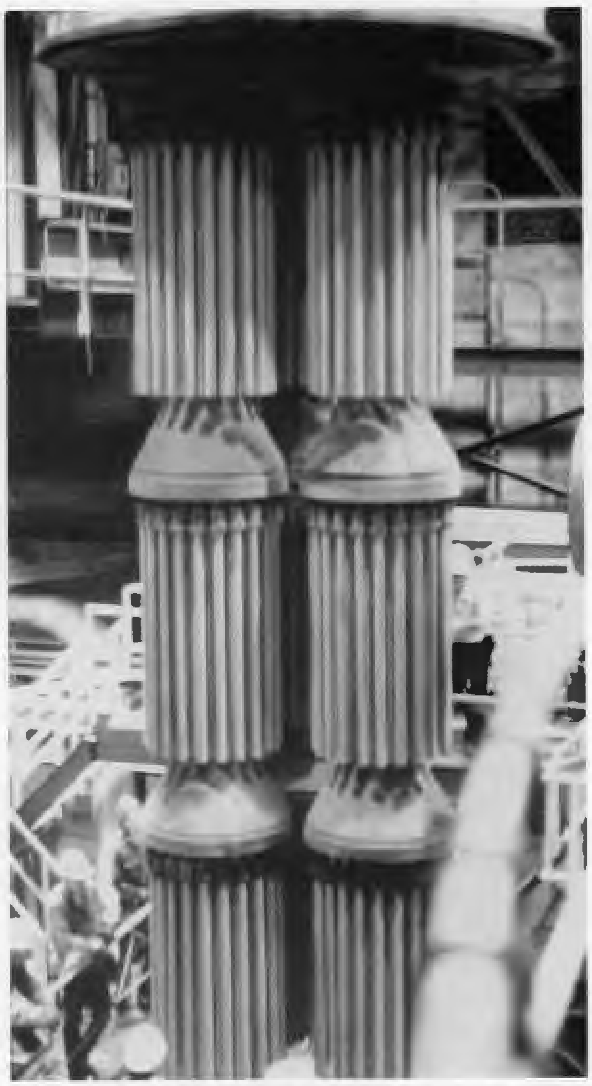
meters (5 feet) long and 6.4 centimeters (2.5 inches) in diameter. So in 1989 the Laboratory issued a request for proposals to filter companies to work with ORNL to design and manufacture filters for testing. Of the eight responses by the competitive bidders, the ORNL scientists were favorably impressed with three. They chose the 3M Company of St. Paul, Minnesota, because of the strength of its proposal and because of its experience in manufacturing and marketing bag filters. Says Stinton: "We thought they were most likely to improve and commercialize our filter concept."

Stinton and his ORNL colleagues began work initially with 3M Company scientist Lloyd White and subsequently worked on improving the filter design with 3M Company scientists Bob Smith, Ed Fischer, Joe Eaton, Bill Weaver, Larry Kahnke, and Doug Pysher. "I initially wanted to coat felt with silicon carbide," Stinton says, "but because of 3M's experience we settled on using a combination of chopped fibers to control porosity and continuous fibers to provide strength and prevent breakage."

The oxide fiber used to fabricate each layer of the filter is a 3M product called Nextel™ 312 that consists of alumina, boria, and silica. The relatively fragile chopped fiber filter surface is covered by an open braid of Nextel™ 312 to protect it during installation and handling. The resulting filter is light, strong, tough, resistant to thermal shock, relatively inexpensive, and easily retrofitted in filter holders.

"In 1990 and 1991, our project with 3M stagnated," Stinton adds. "It was not an initial success. But Rod convinced them that there was this need out there and that our ORNL-3M team was close to having a good filter worth testing. So the work picked up on the project and we produced a filter to test."

The resulting filter is light, strong, tough, resistant to thermal shock, and relatively inexpensive.



This collection of ceramic filters in a combined-cycle power plant removes ash particles from hot gases generated by burning coal, protecting the plant's gas turbine from erosion and corrosion.

In 1992, Stinton and his colleagues received a patent for their filter invention. In September 1994, 3M obtained rights to the ORNL technology through a licensing agreement with Lockheed Martin Energy Systems.

The main U.S. supplier of filter systems for combined-cycle pilot plants is Westinghouse Electric Corporation. But how do you motivate this giant firm to consider testing new filters in its combined-cycle pilot plants? Says Stinton, "With the encouragement and aid of METC's Richard Dennis and the DOE program manager, Jim Carr, ORNL provided money through 3M Company for Westinghouse to test filters on a bench scale at the Westinghouse Science and Technology Center. In March 1993, Westinghouse researchers conducted tests and found that the 3M filters performed as well as other filters. However, the test showed a need for improved filter construction. All parties saw the value of these tests; Westinghouse, 3M, American Electric Power, METC, DOE, and ORNL collaborated to test the filters in a Clean Coal Technology project at the Tidd pressurized fluidized-bed combustor demonstration plant in Brilliant, Ohio. The filters will also be tested in a pilot plant in Alabama, and 60 of the 3M filters were provided for a demonstration plant in Karhula, Finland."

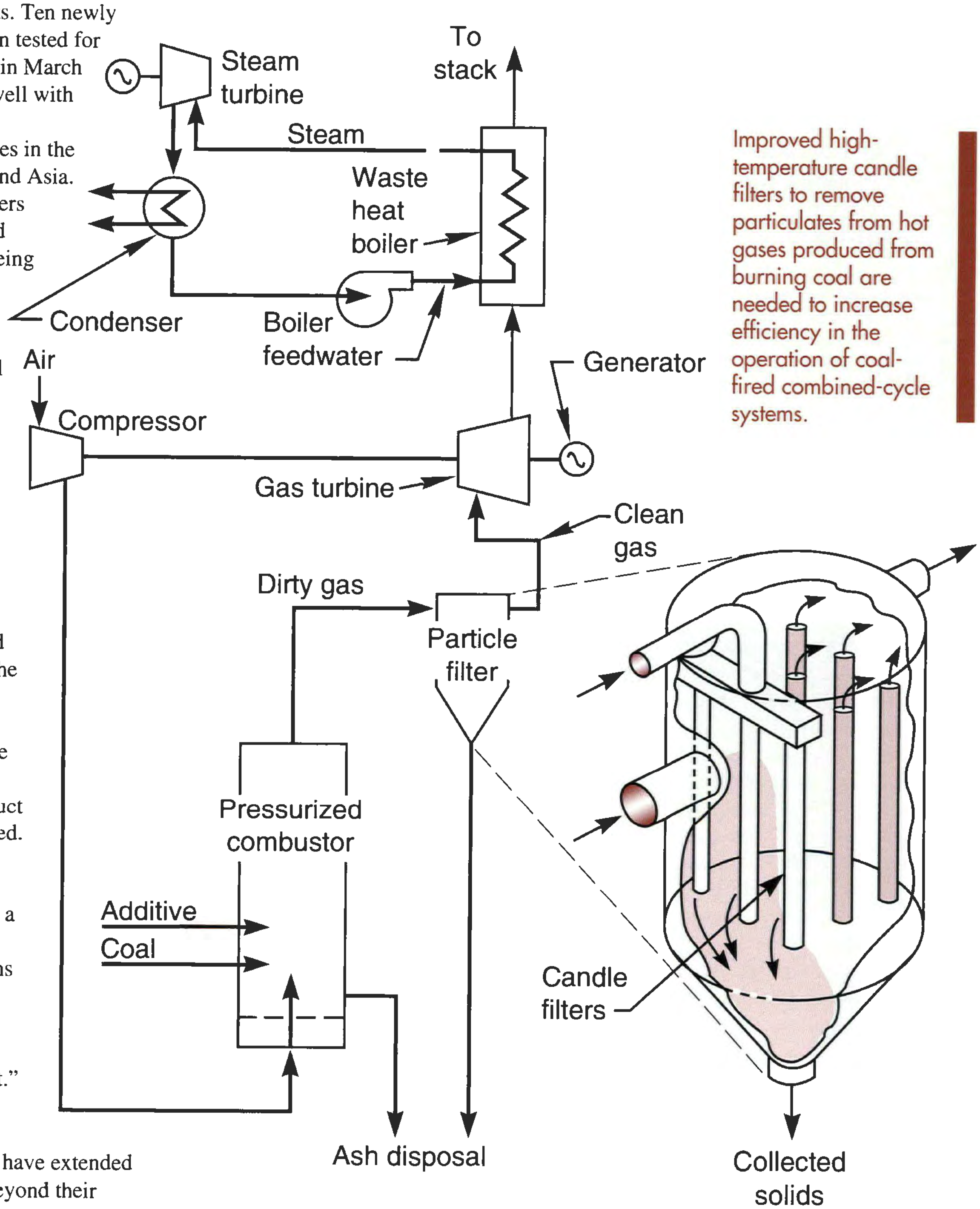
Westinghouse agreed to test three filters in Tidd for 2000 hours. Although two of the three filters failed, it was determined that the failures were not caused by any flaws in the filters. So 3M modified the attachments. Ten newly installed filters were then tested for over 1000 hours ending in March 1995. They performed well with no significant problems.

3M has now made sales in the United States, Europe, and Asia. Improvements in the filters continue to be made, and production capacity is being increased. The filter business is expected to earn $200 million per year by 1998 with a total market of about $7 billion from now to 2003, according to independent estimates.

"Many companies don't like to take risks," Stinton observes. "They have to be helped along. Rod helped 3M see the market, which he learned about from his visits to the combined-cycle pilot plants. He played an important role because he kept encouraging 3M to finish developing a product for which there was a need.

"Technology transfer doesn't mean simply transferring an idea from a national laboratory to a private company. It means having teams from both work together and encourage each other to improve the final product."

"The demanding conditions in these advanced power systems have extended conventional materials beyond their limits of durability," says Judkins, manager of ORNL's Fossil Energy



Improved high-temperature candle filters to remove particulates from hot gases produced from burning coal are needed to increase efficiency in the operation of coal-fired combined-cycle systems.

Program. "We simply had to create a composite material that could better handle those demands."

"Coal-fired power plants will supply a significant portion of world demand for electricity in the coming decades," says Ed Fischer, leader of the 3M hot gas filtration team. "Products such as the 3M ceramic composite filter are critical to the success of advanced coal-fired power generation technologies."

Superconducting Cable Goal of Southwire-ORNL CRADA

ORNL has teamed with the largest U.S. manufacturer of electrical transmission cable to develop a "superconducting cable" that will deliver electricity efficiently. ORNL and Southwire Company of Carrollton, Georgia, are working together to provide this "third-millenium technology."

Superconductivity is the phenomenon in which substances cooled to very low temperatures lose all resistance to electrical current, virtually eliminating energy losses during transmission.

Underground cables are being installed increasingly in dense urban areas and places where right-of-way space is at a premium. Superconducting cables will deliver at least twice as much current as conventional cables, providing energy more efficiently.

"This is one of the most exciting and challenging projects ever undertaken by Southwire," says Roy Richards, Jr., chairman and chief executive officer of company. "The efficient use of energy is critical to our country's future competitiveness, and we are confident we can make a major contribution toward that goal—confident enough, in fact, to invest our own money in the program."

This is one of the most exciting and challenging projects ever undertaken by Southwire.

The two organizations seek to demonstrate the commercial viability of the technology. Under a cooperative research and development agreement (CRADA), DOE will provide $95,000 and Southwire will contribute at least $775,000 in the first phase of what could be a multiphase project.

"This agreement demonstrates DOE's role as broker of one of tomorrow's exciting energy technologies," says Christine A. Ervin, DOE's Assistant Secretary for Energy Efficiency and Renewable Energy. "Through the marriage of two unique American strengths—U.S. private sector entrepreneurial spirit and the unique technological resources of DOE's Oak Ridge National Laboratory—our private-sector partners can become world leaders in high-temperature superconductivity wire and coil manufacture."

Southwire's assignment is to design and fabricate a one-meter (1-m) length of superconducting cable for testing and verification of the project's concept. ORNL will use its unique testing facilities to measure the performance of the cable and will provide cryogenic, or low-temperature, systems support to Southwire.

"If the test cable works, then it should be possible to fabricate much longer lengths and thus commercialize what is now an experimental technology," says R.L. Hughey, project manager for Southwire.

Electrical current will be carried by silver-clad tapes containing dozens of filaments of "high-temperature" superconductor made of a copper oxide ceramic. When chilled by liquid nitrogen to approximately 77 K (–320° F), the tapes lose their resistance to electricity and conduct direct current (dc) with virtually no energy loss. (The technology is considered "high temperature" when compared to the temperature of the much more expensive coolant, liquid helium, which is 4.2 K.)

"Superconductors are loss-free only when carrying dc current," says Martin S. Lubell, an ORNL expert on superconducting magnets. "The transmission cable we are developing with Southwire will be carrying alternating current. Because there will be ac losses, these must be measured and kept low for the cable to be ultimately viable."

Southwire is the nation's largest manufacturer of copper and aluminum rod, wire, and cable for the transmission and distribution of electricity. The company will handle the experimental fabrication of the cable and work with ORNL to design and build test equipment and perform scanning electron microscopy to study the characteristics of materials used in the project.

Bob Hawsey, director of ORNL's Superconductivity Technology Center, is project manager for the ORNL effort. The researchers working on the project are Don Kroeger and Patrick Martin, both of ORNL's Metals and Ceramics Division, and Lubell, Winston Lue, and Ed Jones, a postdoctoral research fellow, all with ORNL's Fusion Energy Division. The DOE funding source is Energy Efficiency and Renewable Energy, Office of Utility Technologies.

The superconducting cable will be fashioned from dozens of individual silver-clad ceramic tapes, purchased by Southwire from Intermagnetics General Corporation. These tapes will be wound around a pipe that carries liquid nitrogen, *ORNL and Southwire are both bringing unique facilities to the project.*

and the insulating material will be wound around the superconducting tapes.

The silver-clad tapes are made by first drawing silver tubes packed with powders of a ceramic compound containing bismuth, strontium, calcium, copper, and oxygen (BSCCO, pronounced "bisco"). The thin silver-clad BSCCO tubes that result are chopped into filaments and stacked into a hollow silver tube that is drawn, rolled, and heated to align the superconducting grains and produce a thin, flat tape.

"The silver-clad BSCCO tapes conduct current well at liquid nitrogen temperatures if they are not exposed to large magnetic fields, such as those required to operate electric motors and generators," Hawsey says. "BSCCO is well suited for the transmission cable application because its current-carrying ability is not greatly affected by the very low fields generated by neighboring wires in the cable."

ORNL's unique testing facilities that will be used for this project include (1) a facility in the Metals and Ceramics Division for measuring the electrical performance of the individual purchased tapes, and (2) a cable alternating-current (ac) loss test facility in the Fusion Energy Division that is capable of measuring the ac losses in 1.25-m-long cables. Says Hawsey: "The cable test facility that has been recently developed and built in the Fusion Energy Division is unique among the national labs."

ORNL's Fusion Energy Division is designing the cryogenic system for the liquid nitrogen–based transmission cables. This system includes the cable cryostat, or insulated jacket, as well as electrical leads and terminations, insulation, and structural designs for operation at 77 K.

"Southwire is also bringing unique facilities to the project," Hawsey says. "These include a high-voltage test lab and a polymer lab for dielectrics-insulation research. Southwire is even lending ORNL a 2000-ampere ac power supply for the cable testing to be done in Oak Ridge."

If the test cable works, will there be any problems with manufacturing longer lengths for commercial purposes?

"Several issues must be resolved to scale-up the superconducting cable to longer lengths," Hawsey says. "Challenges in the second phase of the project include cable manufacturing machinery design (because the superconducting tapes are fragile), cryogenic dielectric and insulation design, and cooling system design. In addition, the cost of today's research-grade tapes must decrease 10 to 100 times, and tensile strength must increase 3 to 5 times, for the cable to be commercially viable. However, there are no known technical show-stoppers, at this time. We hope to have a Southwire utility customer on the team for the second phase to help us design and test the long-length cables."

Teamwork will remain a key to developing new technologies for the third millenium. **ornl**

The first Southwire Company superconducting cable for an underground transmission line is prepared to go into a dewar for critical current and ac-loss measurements at liquid nitrogen temperature (77 K). The measurements are performed by the Magnetics and Superconductivity Group of ORNL's Fusion Energy Division. The cable is wound with four layers of thin high-temperature superconducting tape manufactured by Intermagnetics General Company.

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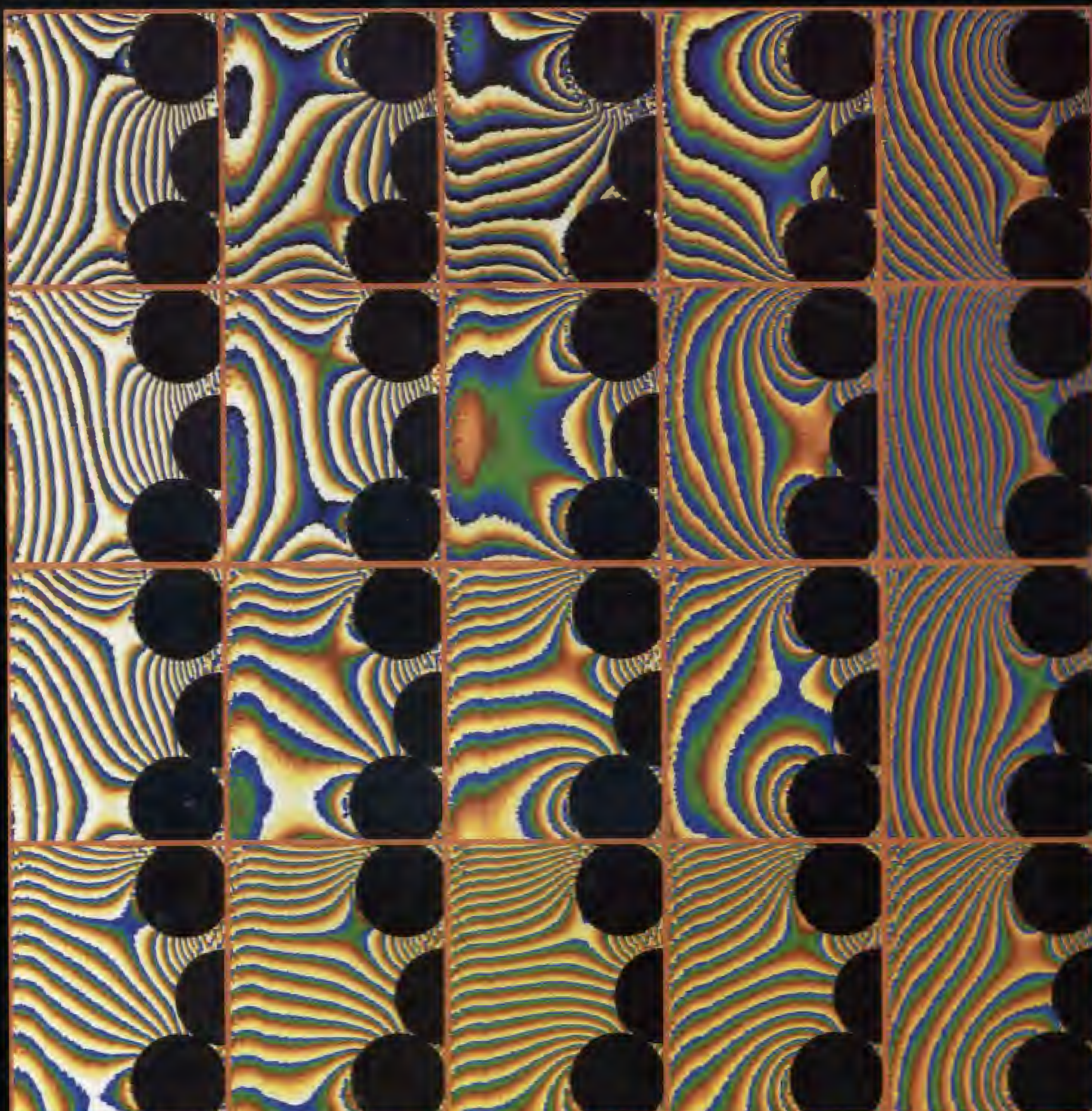

Distribution of electric field lines surrounding three 2.7 micrometer diameter latex spheres charged by an electron beam, recorded using electron holography. The various images of the tableau are obtained mathematically by viewing the reconstructed phase from different angles. Electron holography at ORNL is described in an article on p. 38.