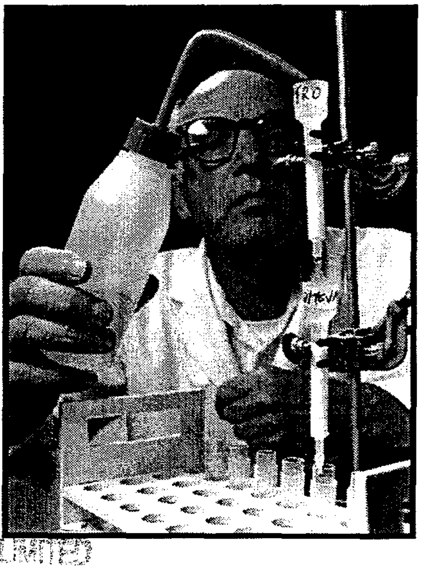
ANL/ES/PC--92669

Chemical Research at Argonne National Laboratory

Information Systems

Supply Chain Technology

Manufacturing and Operations



New Chemical Science and Engineering Technology

A U.S. Department of Energy Laboratory

Argonne National Laboratory is operated by the University of Chicago for the U.S. Department of Energy.

Overview

Argonne National Laboratory is a research and development laboratory located 25 miles southwest of Chicago, Illinois. It has more than 200 programs in basic and applied sciences and an Industrial Technology Development Center to help move its technologies to the industrial sector.

At Argonne, basic energy research is supported by applied research in diverse areas such as biology and biomedicine, energy conservation, fossil and nuclear fuels, environmental science, and parallel computer architectures. These capabilities translate into technological expertise in energy production and use, advanced materials and manufacturing processes, and waste minimization and environmental remediation, which can be shared with the industrial sector.

The Laboratory's technologies can be applied to help companies design products, substitute materials, devise innovative industrial processes, develop advanced quality control systems and instrumentation, and address environmental concerns. The latest techniques and facilities, including those involving modeling, simulation, and high-performance computing, are available to industry and academia. At Argonne, there are opportunities for industry to carry out cooperative research, license inventions, exchange technical personnel, use unique research facilities, and attend conferences and workshops.

Technology transfer is one of the Laboratory's major missions. High priority is given to strengthening U.S. technological competitiveness through research and development partnerships with industry that capitalize on Argonne's expertise and facilities.

The Laboratory is one of three DOE superconductivity technology centers, focusing on manufacturing technology for high-temperature superconducting wires, motors, bearings, and connecting leads.

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For information on technology transfer working arrangements, contact Argonne's Industrial Technology Development Center at 800/627-2596.

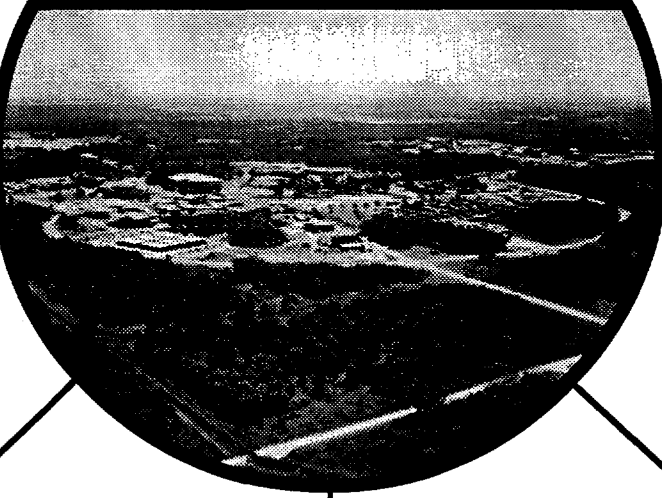
Argonne National Laboratory

Design, Construction, and Operation of Large Accelerator-Based User Facilities and Related Technologies

Integration of a Broad Science and Engineering Base into the Development and Evaluation of Nuclear and Other Advanced Energy Technologies

Conducting Large-Scale, Integrated Research Programs in Materials Sciences, Chemical Sciences, and Mechanistic Biology

CORE COMPETENCIES



Assessing, Developing, and Testing Energy-Efficient Industrial, Transportation, and Other End Use Technologies

Application of Modeling, Simulation, and Advanced Computing and Communications to Study Complex Systems and Phenomena

Integration of Environmental Research, Development, Assessment, and Remediation

Planning and Implementing R&D Partnerships with Industry and Universities to Address Problems in Primary Mission Areas

Educating and Training Future Scientists and Engineers by Using Frontier Research Techniques and Facilities

SCIENCES

Materials Sciences

Superconductivity	● ▲ ◆ ★ ◉ ⛊
Magnetic Materials	● ▲ ◆ ★ ◉ ⛊
Surface and Interface Studies	■ ● ▲ ★ ◉ ⛊
Radiation Effects	■ ▲ ★ ◉ ⛊
Neutron and X-ray Diffraction and Scattering	▲ ★ ◉ ⛊
Analytical and Transmission Electron Microscopy	▲ ★ ◉ ⛊
Laser Resonance Spectroscopy	▲ ★ ◉ ⛊
Thin-Film Materials	▲ ★ ✚ ◉ ⛊

Chemical Sciences

Photosynthesis	▲ ◉ ⛊
Coal Science	▲ ◉ ⛊
Heavy-Element Separation Science	■ ▲ ✚ ◉ ⛊
Electron- and Photon-Stimulated Fast Chemistry	▲ ◉ ⛊
Theoretical Chemical Dynamics	▲ ★ ◉ ⛊
Cluster Chemistry	▲ ★ ◉ ⛊

Biosciences

Computational Biology	▲ ★ ◉ ⛊
Structural, Cellular, and Molecular Biology	▲ ◉ ⛊
Genome Sequencing	▲ ◉ ⛊
Bioprocessing	▲ ✚ ◉ ⛊
Ecology	★ ✚ ◉ ⛊

Synchrotron Radiation Techniques

Biostructure Determination	▲ ◉ ⛊
Time-Dependent Materials Characterization	▲ ◉ ⛊
Lithography	▲ ◆ ◉ ⛊
Atomic Physics and Surface Science	▲ ◉ ⛊
Advanced X-ray Optical and Detection Techniques	● ◉ ⛊
Synchrotron Radiation Sources	● ▲ ★ ◉ ⛊

Mathematics and Computer Science

Linear Algebra and Optimization	★ ◉ ⛊
Automated Reasoning	■ ★ ◉ ⛊
Codes for Massively Parallel Architectures	■ ▲ ★ ◉ ⛊
Algorithms for Computational Science and Engineering	■ ▲ ★ ◉ ⛊
Modeling, Simulation, and Visualization for Energy and Industrial Technologies	■ ● ▲ ◆ ★ ✚ ◉ ⛊

Information Sciences

Information Retrieval	★ ✚ ◉ ⛊
Advanced Communication Technologies	★ ◉ ⛊
Database Management	★ ✚ ◉ ⛊

Accelerator Physics and Technology

Accelerator Systems and Design	● ▲ ★ ◉ ⛊
RF Superconducting Technology	● ◉ ⛊
Advanced Particle and Photon Detectors	● ▲ ★ ◉ ⛊
Magnetic Field Measurement and Analysis	■ ● ★ ◉ ⛊
RF and High-Voltage Power Systems	● ★ ◉ ⛊

High Energy and Nuclear Physics

Particle Physics	★ ◉ ⛊
Heavy-Ion Physics	★ ◉ ⛊

National Research Facilities

Advanced Photon Source	● ▲ ◆ ◉ ⛊
Intense Pulsed Neutron Source	● ▲ ◉ ⛊
Argonne Tandem Linear Accelerator System	● ◉ ⛊
High-Voltage Electron Microscope Facility	■ ● ▲ ◉ ⛊
Hot Fuel Examination Facility	■ ◉ ⛊
Experimental Breeder Reactor II	■ ★ ◉ ⛊
Transient Reactor Test Facility	■ ★ ◉ ⛊
Fuel Cycle Facility	■ ★ ◉ ⛊
Alpha-Gamma Hot Cell Facility	■ ◉ ⛊
Structural Biology Center	▲ ◉ ⛊
High-Performance Computing Facility	■ ★ ◉ ⛊

TECHNOLOGIES

Advanced Nuclear Technology

Reactor Design and Analysis	■ ★ ◉ ⛊
Reactor Decommissioning/Decontamination	■ ✚ ◉ ⛊
Reactor Safety Tests and Analysis	■ ★ ◉ ⛊
Nuclear Fuels and Materials	■ ★ ◉ ⛊
Nuclear Waste Treatment Technology	■ ★ ◉ ⛊
Research and Test Reactors	■ ★ ◉ ⛊

Energy Supply Systems

Fusion Reactor Technologies	■ ● ★ ✚ ◉ ⛊
Coal Combustion and Gasification	■ ◉ ⛊
Heat and Mass Transfer	■ ◆ ★ ◉ ⛊

Engineered Materials

Metals and Metallic Alloys	■ ● ▲ ◆ ◉ ⛊
Ceramics and Ceramic Composites	■ ▲ ◆ ◉ ⛊
Polymers and Polymer Composites	■ ▲ ◆ ◉ ⛊
Coatings and Surfaces	■ ▲ ✚ ◉ ⛊
Environmental Effects	■ ◆ ✚ ◉ ⛊
Advanced Sensors and Sensor Materials	■ ● ▲ ◆ ✚ ◉ ⛊
Superconductors for Power Applications	▲ ◉ ⛊
Surface Modification	● ▲ ◉ ⛊
Corrosion, Erosion, Friction, and Wear of Engineered Surfaces	■ ▲ ◆ ✚ ◉ ⛊
Mechanical Behavior and Life Prediction	■ ▲ ◆ ★ ◉ ⛊
Liquid Metal Technologies	■ ◉ ⛊

Industrial Technologies

Instrumentation and Nondestructive Evaluation of Materials and Systems	■ ● ▲ ◆ ◉ ⛊
Pyro- and Electrochemical Processing	■ ▲ ◆ ◉ ⛊
Energy Storage and Cogeneration	■ ◆ ◉ ⛊
Thermal and Fluid Sciences	■ ◆ ★ ◉ ⛊
Engineering Mechanics and Mechanical Behavior of Structures and Components	■ ● ▲ ◆ ★ ◉ ⛊
Process Efficiency and Waste Recycling	◆ ✚ ◉ ⛊
Control Systems	■ ● ◆ ★ ◉ ⛊
Biotechnology	▲ ✚ ◉ ⛊
Ultra-High Vacuum Science and Technology	■ ● ★ ◉ ⛊

Transportation Systems

Batteries and Fuel Cells for Electric Vehicles	▲ ◆ ◉ ⛊
Maglev Systems Design, Analysis, and Testing	◆ ◉ ⛊
Advanced Vehicles	◆ ◉ ⛊
Alternative Fuels	◆ ◉ ⛊

Systems Analysis, Technology Assessment, and Decision Sciences

Economics, Law, and Policy Analysis	■ ◆ ◉ ⛊
Arms Control and Nonproliferation	■ ◉ ⛊
Emergency Systems	■ ● ◆ ◉ ⛊
Probabilistic Risk Analysis	■ ✚ ◉ ⛊
Expert Systems for Artificial Intelligence	■ ★ ✚ ◉ ⛊
Planning for Utility and Other Energy Systems	■ ◆ ◉ ⛊
Engineering Analysis and Cost Estimation	■ ● ◆ ★ ◉ ⛊
Environmental Policy and Regulatory Analysis	■ ● ◆ ✚ ◉ ⛊

Environmental Science and Technology

Environmental Control Technology	■ ✚ ◉ ⛊
Nuclear Waste Management	■ ✚ ◉ ⛊
Rapid Site Characterization	✚ ◉ ⛊
Land Reclamation	✚ ◉ ⛊
Environmental Pathways Modeling and Measurement	★ ✚ ◉ ⛊
Natural Resource Impacts: Evaluation and Remediation	✚ ◉ ⛊
Atmospheric Sciences and Climate Change Modeling	★ ✚ ◉ ⛊
Inorganic and Isotopic Geochemistry	▲ ✚ ◉ ⛊
Analytic Geographic Information Systems	★ ✚ ◉ ⛊
Health Risk Assessment	★ ✚ ◉ ⛊

Contents

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Notation

AASB	analytical activated bauxite sorber bed
ABS	aqueous biphasic separation
ACL	Analytical Chemistry Laboratory
AES	Auger electron spectroscopy
ALICE	Arbitrary Lagrangian Implicit Continuous-Fluid Eulerian
ANL	Argonne National Laboratory
APS	Advanced Photon Source
cermet	ceramic metallic
CVD	chemical vapor deposition
DIPHONIX	diphosphonic acid exchange
DLC	diamond-like carbon
EPR	electron paramagnetic resonance
FBC	fluidized-bed combustor
FBR	fluidized-bed reactor
FIA	flow injection analysis
FLUSTR	Fluid Structure Interaction Code
FTIR	Fourier-transform infrared
GC/MI-IR	gas chromatography/matrix-isolation/infrared spectroscopy
GTM	Generic TRUEX Model
HEU	high-enriched uranium
IPNS	Intense Pulsed Neutron Source
LEU	low-enriched uranium
LIGS	laser-induced grating spectroscopy
LWRs	light-water reactors
MADS	membrane-assisted distillation system
MAG*SEP	magnetic separation
MASX	membrane-assisted extraction
MHD	magnetohydrodynamic
MIC	microbiologically influenced corrosion
MRI	magnetic resonance imaging
NMR	nuclear magnetic resonance
OGMS	open gradient magnetic separator
PSA	probabilistic safety analysis
RC	reinforced concrete
SSRT	slow strain rate tensile
TRU	transuranics
TRUEX	transuranium extraction
VOCs	volatile organic compounds

Introduction

This booklet provides information on Argonne National Laboratory's (ANL's) research in areas related to the chemical industry. The projects described demonstrate the Laboratory's technical and engineering capabilities in the four technical disciplines identified by the Technology and Manufacturing Competitiveness Task Group[1] as crucial to the future of the chemical industry:

- New Chemical Science and Engineering Technology
- Supply Chain Technology
- Information Systems
- Manufacturing and Operations

TABLE 1 Keywords for Searching the ANL Programs/Capabilities Database

Adsorption
Alloys
Analytical
Battery
Biotechnology
Catalysis
Catalyst
Ceramics
Coatings
Corrosion
"Database Management"
Desorption
Diamond
Dyes
Electrochemistry
Environment
Environmental
Enzymes
Fabrication
"Fluidized Bed"
"Fuel Cells"
"Information Management"
Kinetics
Lubrication
Materials
Metals
Mechanisms
Oil
Paints
Particles
Petrochemical
Plasma
Plastics
Polymer
"Process Control"
"Process Development"
"Process Modeling"
"Process Monitoring"
Production
Properties
"Reaction Modeling"
Readiness
Risk
Resins
Safety
Sensors
Separation
Superconductor
Surface
Surfactants
Synthesis
Thermochemistry
Tribology
Vitrification
VOC
Waste

Note — Two-word keywords must be entered in quotes " " as shown in the table. Otherwise the search will generate a list of all projects containing one of the two words.

Over 375 projects were selected from the Argonne Programs/Capabilities Database on the Web (http://www.anl.gov/LabDB/anlprogcap.html) using the keywords listed in Table 1. In selecting the projects for discussion, we attempted to address the four disciplines identified and the specific technical areas discussed in the Vision 2020[1] document. While several of Argonne's

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[1] "Vision 2020 . . . . . ., The U.S. Chemical Industry, The Industry's View of the Direction for the Future," prepared by the Technology and Manufacturing Competitiveness Task Group, May 1996.

capabilities — such as designing and operating nuclear plants using expert systems that are based on fuzzy logic and neural network technologies — were originally developed for U.S. Department of Energy (DOE) sponsors, they could be readily adapted to chemical process control. Both DOE- and U.S. Department of Defense (DoD)-sponsored projects related to information/database management systems could be used for inventory control, decision support, and supply chain management in the chemical industry.

The selected projects were divided into three main areas — Basic Science, Information Management, and Unit Operations — and then into more specific areas of research, as outlined in Table 2. The shaded cells of the table show how these areas of Argonne's expertise relate to the four technical disciplines listed above. Each brief description of our research capabilities includes index numbers **(nnn-nnn)** from our database for individual projects that illustrate that capability. If you would like more information about a specific project or projects, please contact the Industrial Technology Development Center at (800/627-2596) or visit our web page at the above address and search the database for the desired project by entering its index number (note that this search engine requires that the index number be entered within quotes, i.e, "599-002".

TABLE 2 Comparison of the Chemical Industry's Vision 2020 and Argonne's Areas of Expertise

Argonne's Areas of Expertise	Chemical Industry's Vision 2020			
	New Chemical Science and Engineering Technology	Supply Chain Technology	Information Systems	Manufacturing and Operations
Basic Science				
Chemical Research	■			
Electrochemistry	■			
Biothechnology	■			■
Catalysis	■			■
Materials	■			■
Environmental Chemistry	■			■
Petrochemistry	■			■
Information Management				
Advanced Process Design and Analysis	■		■	■
Safety	■		■	■
Data Management		■	■	■
Unit Operations				
Separations	■			■
Heat Transfer	■			■
Sensors	■			■
Analytical Chemistry	■			■

Because forming R&D partnerships with the national laboratories is one of the major recommendations of the Vision 2020 document,[1] we recommend that you read the following publications to obtain information on participating in cooperative research projects with Argonne: *How Federal Agencies Obtain Technical Resources and Skills from the U.S. Department of Energy*, *How Private Customers and Nonfederal Governments Obtain Technical Resources and Skills from the U.S. Department of Energy*, and *Argonne National Laboratory: Strong Commitment to Increased U.S. Economic Competitiveness*. Please call ANL's Information and Publishing Division ([630] 252-6064) to receive copies of these publications.

Basic Science

Chemical Research

Chemistry has been a core capability of Argonne National Laboratory since the Laboratory was founded 50 years ago to explore the peaceful uses of atomic energy. Argonne is now a multidisciplinary research center dedicated to solving energy-related scientific and engineering problems confronting the nation. Argonne's diverse staff of scientists and unique instrumentation allow us to quickly assemble multidisciplinary teams to meet these challenges. The following is an introduction to the chemical sciences at Argonne National Laboratory.

Fundamental Chemical Processes

Argonne's radiation and photochemistry group addresses the chemistry of short-lived radicals and radical ions and the roles of solvents and matrices in modulating their reactivity. Lasers and a 20-MeV electron linac provide the ultrashort energy pulses required to conduct this research. The program has led to many basic discoveries, including the solvated electron and the role of ion radicals as intermediates in reaction chemistry **(201-005)**, and to a better understanding of catalysis in zeolite reactors **(205-001)**. Argonne scientists have also found that radiation chemistry mechanisms are responsible for processes that result in radiation damage and for many uses of radiation in industrial processing **(196-002)**.

The electron transfer, energy conversion, photochemical conversion, and molecular photonics groups are characterizing the basic principles that control charge separation in electron transfer reactions molecular systems. Combinations of linac and laser excitation enable the scientists to study within many novel structures; remarkable progress has been made in this area since the first demonstration of the Marcus inverted region at Argonne. Theoretical models are also being developed to complement and extend the experimental work. Many techniques are used to study charge transfer dynamics, including time-domain electron paramagnetic resonance and femtosecond optical spectroscopy. Argonne chemists first identified the special chlorophyll pair in the natural photosystem and built on this

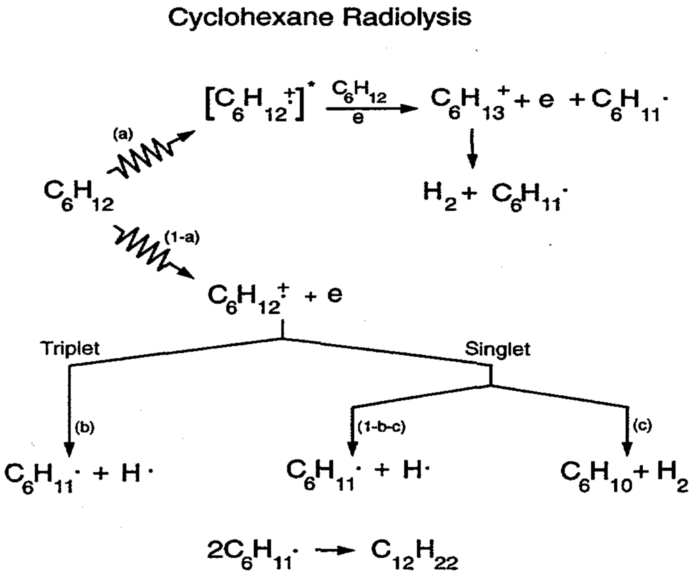

FIGURE 1 Energetic radiation can influence the course of chemical reactions **(196-002)**

breakthrough to develop a fundamental understanding of photochemical electron transfer. This understanding allowed the researchers to prepare organic molecular systems that carry out high-efficiency, light-initiated charge separation and long-lived energy storage in the solid state **(103-002, 103-003)**. It also led to the potential to produce new materials for solar energy collection and storage **(121-001)**.

Argonne scientists are using the knowledge gained from studies of electron transfer within organic donor-acceptor molecules to develop ultrafast opto-electronic devices for use in signal processing, optical computing, and sensor applications. The successful design and production of energy-efficient, state-of-the-art electronic devices depend increasingly on the ability to produce ever-higher densities of circuit elements within integrated circuits. The development of molecular electronics that use molecules as switches, wires, microsensors for chemical analysis, and components in optical computing devices is a rapidly growing enterprise. The first type of molecular switch developed at Argonne employs two electron donors that can each transfer an electron to a common two-electron acceptor **(115-001, 116-001, 119-001, 123-002)**.

Argonne is using a variety of laser techniques based on resonant-enhanced multiphoton ionization, mass spectrometry, photoelectron spectrometry, and fluorescence spectrometry to investigate the spectroscopy and decay dynamics of molecules in highly excited states. The importance of this work lies in the areas of advanced laser technology for chemical measurements and ultrasensitive detection, excited-state radiation physics and chemistry, and measurement science **(079-005, 122-001, 153-001)**.

Computational Chemistry

Argonne is a leader in the development of new codes to exploit massively parallel machines for solving chemical problems. Argonne's research on chemical dynamics merges theoretical and experimental work to establish the energetics and dynamics of chemical reactions. Very special facilities at Argonne — such as the IBM Scalable POWER Parallel™ computer — permit state-of-the-art theoretical and computational work. Integrated experimental studies are conducted in parallel by Argonne scientists on state-selective chemistry, the chemical kinetics of radical-radical reactions, and photoionization spectroscopy to test new concepts of chemical reactivity. We are also exploring diverse applications, including superconductor modeling, electromagnetic design modeling, computational chemistry, and modeling of the dynamics of complex mechanical systems **(047-001, 079-008)**. Our work includes using state-of-the-art electronic structure techniques to accurately predict the thermodynamic properties of small-molecule reactions that are important to hydrocarbon combustion (i.e., heats of formation, geometries, and vibrational frequencies), determining rates of reaction (including temperature and pressure dependencies), performing calculations of organic superconductors, and providing new insight into the action of clays (e.g., zeolites) as catalysts **(090-001)**.

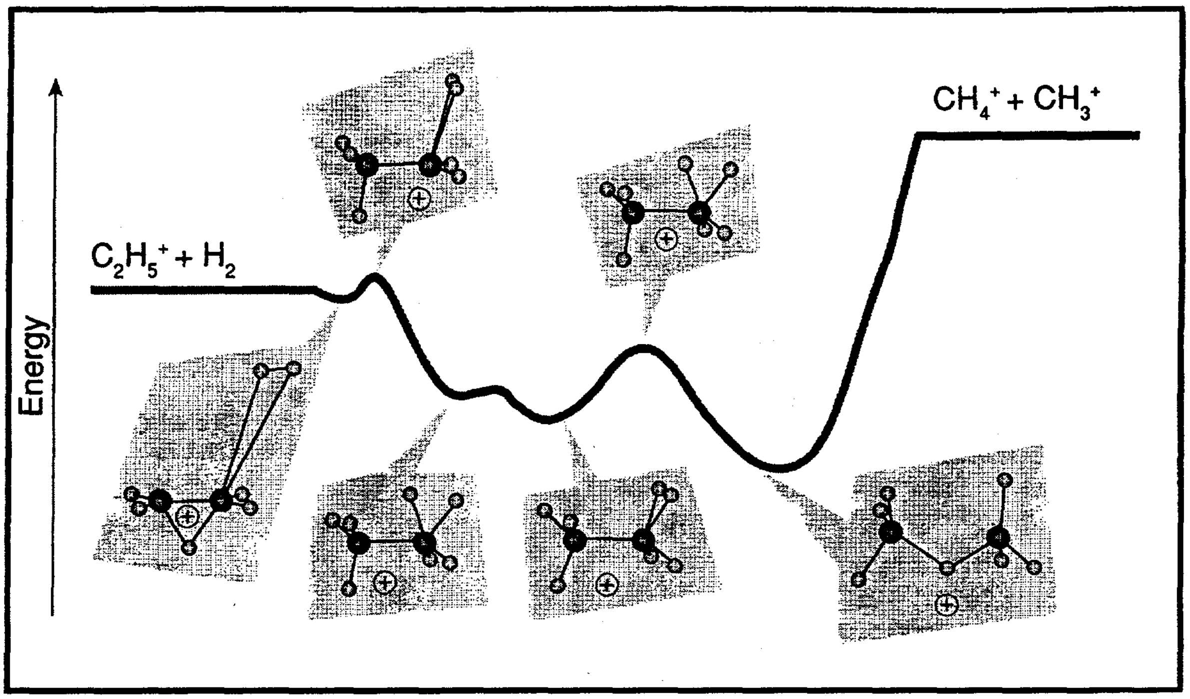

FIGURE 2 Calculated changes in potential energy for reaction of $C_2H_5^+$ with H_2 **(078-016)**

The quantum chemical studies at Argonne concentrate on the development of first principles ab initio molecular orbital computational methods. This work includes the widely acclaimed Gaussian-2 method for determining the molecular energies of compounds composed of light elements **(000-008)**. Argonne has many unique facilities to complement the computational studies. For instance, the Laboratory has the only shock tube facility in the world capable of measuring the thermal rate coefficients and branching ratios of elementary reactions within the first 10 microseconds of the experiment at high temperatures. Flash photolysis-shock tube studies are used to measure thermal gas phase rate constants using the high temperatures available with shock wave heating. We have applied these techniques to a large variety of chemical systems relevant to combustion (e.g., O with H_2, C_2H_2, H_2O, CH_3) and incineration (e.g., thermal decompositions of CH_3Cl, CH_2Cl_2, $CHCl_3$, CCl_4, CF_3Cl, $COCl_2$) research **(191-001, 079-002, 079-003, 040-002, 079-004, 079-006, 079-007)**.

Surface Science

Argonne's surface science research team explores the chemistry and physics of surface properties **(010-005)**. During the last ten years, there has been a major technological emphasis on studying the properties of organic monolayers on inorganic substrates. These structures have a variety of applications — from microscopic adhesion to microlithography. They have also been used to study the functions of biochemical complexes. Argonne is exploring the uses of covalently bound, self-assembled monolayers from alkyltrichlorosilanes. Modification of the alkyl tail permits researchers to tailor surface properties to a specific application; we are investigating the effect of such surface modification on catalytic and barrier properties **(177-001)**.

Fossil Fuel Chemistry

FIGURE 3 Fine-scale chemical heterogeneity in coal is highlighted by differences in absortivity (154-001)

The coal chemistry program seeks to characterize the structure and chemistry of Argonne premium coal samples **(161-001)**, petroleum resid, and heavy crudes both on a global basis and at the molecular level. The members of this research team investigate vital issues, including ecosynthesis, hydrogen atom transfer, and pathways by using a broad array of powerful instrumental techniques including multidimensional nuclear magnetic resonance (NMR) spectroscopy and imaging; synchrotron X-ray spectroscopy, imaging, and scattering; neutron scattering; and laser desorption, high-resolution, and tandem mass spectrometry. The fundamental information derived from these studies will be used to guide the development of new processes to exploit the energy derived from coal, the nation's largest fossil fuel resource **(154-001)** and to improve heavy oil processing **(158-001)**.

Metals Chemistry

The heavy element chemistry group and the separation sciences group are closely linked to enable joint investigations on environmental restoration and waste management. Members of these groups are currently studying new classes of environmentally acceptable water-soluble complexing agents for actinide and lanthanide metal ions and photochemical and photocatalytic methods for destroying these complexants **(152-001)**.

Wavelength-tunable pulsed and continuous-wave lasers are used as sources of fluorescence excitation (from the ultraviolet into the near-infrared) to investigate the photophysics of species present in gas, liquid, and solid phases at temperatures ranging from 1.5 K to 1100 K. Researchers can investigate radioactive and chemically hazardous materials at levels as low as a single atom or molecule. The current emphasis is on actinide-containing materials **(150-001)**.

Unique facilities operated by the separation sciences and heavy element chemistry groups allow Argonne to work with samples containing radioactive material at levels ranging from hot to tracer. These laboratory facilities are available for a wide array of experiments, including thermochemical and kinetic characterization of reactions in solution **(101-001)**. Argonne has also designed and built a laboratory that can handle tritium and tritiated materials with loadings from microcurie to curie levels **(641-001)**.

The metal cluster group investigates the mesophase with special emphasis on transition metal clusters. Argonne achieved an important breakthrough in this area by demonstrating that these metal clusters could be prepared and investigated in the gas phase. Now closely linked experimental and theoretical studies are being conducted to elaborate on the relationship between structure and catalytic activity **(185-001)**.

As part of another experimental program, Argonne is exploring novel applications of synchrotron X-ray scattering and spectroscopy techniques to study chemical processes at mineral-fluid interfaces. One unique facility employed in this research is the synchrotron light source. The goal of this new program is to gain a better understanding of fundamental atomic-scale processes in rock-water systems. Applications are in low-temperature geochemistry and contaminant transport **(177-001, 338-004)**.

Electrochemistry

Electrochemical programs at Argonne focus generally on one of four areas: electrochemical power sources (i.e., batteries, fuel cells, and ultracapacitors [**456-005**]), metals refining, high-temperature superconductors, and organic superconductors. Research projects in each of these areas include technology and materials development, modeling, and testing/demonstration. Some projects (see Materials section) involve fabricating and evaluating organic superconductors and performing basic studies of corrosion.

Batteries and Fuel Cells

This research area includes development of advanced batteries such as lithium polymer **(078-026)**, lithium-ion, sodium/nickel chloride, and lithium/iron sulfide batteries **(012-002)**. Argonne also conducts closely related research on other electrochemical devices, such as sensors; works to solve manufacturing issues involving deposition, mass transfer **(078-025)**, kinetics, and thermodynamics; and develops novel electrode materials to make rechargeable lithium batteries **(012-001, 078-027)**. Our specialties include experimental and theoretical aspects of electrochemical engineering, computer modeling (mainframes to PCs), data acquisition and control, and data analysis and problem solving. The Laboratory is equipped with fully automated instrumentation, including digital data acquisition and analysis instruments **(322-002)**, that is used for analysis and diagnosis of electrochemical systems, such as batteries, fuel cells, electrolyzers, and electrochemical processes. In the Analysis and Diagnostics Laboratory (ADL) users facility, advanced battery systems and fuel cells have been tested under simulated applications since 1976 **(456-003, 460-003)**. After testing, failed cells undergo post-test analyses **(456-002)** to assess component reliability, correlate operational performance with material changes, evaluate failure modes, correlate changes in electrode structures with changes in cell performance, and measure impurities, corrosion, and other forms of component degradation. The ADL provides battery developers with the tools for unbiased assessment of battery performance and life for electric vehicles **(698-001)**, utility load leveling, and uninterrupted power source applications. Special sensors available at ADL enable researchers to conduct malfunction analysis of electrochemical cell components and time-domain analysis of cell processes.

ANL is a leading national laboratory in fuel cell research and development **(460-001)** and supports DOE in managing the fuel cell transportation program. This effort includes development of solid oxide **(460-002)**, molten carbonate, polymer electrolyte **(700-001)**, and phosphoric acid fuel cells. The solid electrolyte fuel cells, which operate directly on hydrocarbon fuels, are being developed for transportation applications; the liquid electrolyte fuel cells will be used for power generation. Argonne fuel cell research and development capabilities include systems analyses, electrochemical characterization, materials development, and design and fabrication of innovative fuel cells. The Laboratory is also working to develop materials for high-temperature sealants for the solid-oxide fuel cell **(460-002, 503-001)** used for anode electrocatalysts. The sealants will allow direct oxidation of liquid hydrocarbon fuels in polymer electrolyte fuel cells.

Battery and fuel cell research requires a thorough knowledge of solid-state chemistry — especially structure/property relationships in inorganic materials — as well as an understanding of transition-metal oxide intercalation compounds, particularly oxides of vanadium, manganese, and nickel. The research also requires validated heat transfer analyses **(213-003)** during duty cycling for nickel metal-hydride and lithium/iron-disulfide batteries and to test electrode performance **(456-004)**.

Recent accomplishments in the fuel cell program include the following: (1) development of a sodium/nickel chloride battery with high power and energy **(456-001)** for use in commercial and special electric vehicles and for electrical network load leveling, and (2) creation of a bipolar lithium/iron sulfide battery stack **(698-001)** that offers electric vehicle performance comparable to that of internal combustion engine vehicles and provides high-power capabilities for use in hybrid electric vehicle applications.

Electrorefining

Argonne has extensive experience in all aspects of electrorefining — including process development capabilities **(100-002)** and supporting analytical work **(265-001)**. Process development efforts focus on the microscale synthesis and characterization of actinide coordination complexes as solids and solution species. These complexes are important for separating, recovering, or isolating actinides from other elements. Glove boxes and inert-atmosphere enclosures are used to handle these highly radioactive materials. Thermochemical, electrochemical, crystallographic, and spectroscopic studies are conducted to characterize the oxidation-reduction, acid-base, and coordination properties of actinide (e.g., uranium and plutonium) species in environments that simulate nuclear-waste conditions.

Argonne has created state-of-the-art computer codes for analyzing multidimensional potential field, current distribution, surface overpotentials, heat transfer, mass transfer, and fluid mechanics in complex electrochemical systems. Applications include analysis of electrowinning (e.g., lithium from lithium oxide in lithium chloride), molten carbonate fuel cells, and polymer electrolyte membrane fuel cells **(265-001)**.

In an electrorefining process developed at Argonne **(644-001)**, metallic actinides from spent nuclear fuel (combined with numerous fission product metal impurities) are incorporated into the anode of an electrorefining cell containing a molten salt electrolyte. When current passes through, purified uranium metal is deposited on a solid metal cathode. Purified plutonium, other transuranics, and uranium are deposited in a liquid cadmium cathode. Metal impurities are either left behind in the anode or form stable halides, which become part of the cell electrolyte **(435-002)**.

A new technology for recycling the galvanized steel scrap found in car and truck bodies into clean scrap could result in an annual savings of $142 million in raw materials for the iron and steel industries. An electrochemical process dissolves and recovers the zinc coating from galvanized steel surfaces. Now being tested at a pilot plant in East Chicago, Indiana, the technology is being developed through a cost-sharing program between Metal Recovery Industries U.S., Inc., and Argonne **(640-004)**.

High-Temperature Superconductors

ANL's capabilities in high-temperature superconductors **(010-004)** range from materials synthesis and processing to sophisticated properties measurement **(391-004)** that involves using links to microstructural studies and phenomenological modeling. The primary focus areas in the program are: (1) the study of fundamental properties of single crystals, thin films, and bulk materials; (2) the synthesis of superconducting compounds, fabrication of conductors, and characterization of resultant microstructures and electrical, physical, and mechanical properties; and (3) the design, fabrication, and testing of superconducting components and systems. These program efforts include both fundamental research and development/commercialization. ANL is developing and validating computational models to simulate the performance of superconducting materials, enhancing flux pinning by controlling fine-scale crystal defects **(390-001)**, and improving the mechanical properties of high-temperature superconductors **(391-002)** by selecting alloys and controlling fine-scale phase development through the manipulation of reaction kinetics. ANL has also developed a substantial database of the physical properties of high-temperature superconductors **(391-003)** in an effort to optimize their performance and processing methods.

Development/commercialization efforts include improving synthesis methods to produce high-temperature superconductors from commercially available materials **(473-001)**. This is achieved by developing and evaluating fabrication techniques to continuously form superconductors into rods, bars, thick films, wires, tapes **(473-002, 566-002)** (with critical current density [J_c] values greater than 200,000 A/ cm^2 at 77 K), and leads for them **(569-001)**. In order to measure the critical current densities of high-temperature superconductors, we have constructed a 1,200-A direct current source **(391-001)** and developed robust, low-resistance contacts. We have also demonstrated microchannel cooling techniques for high-temperature superconducting magnets by using sub-cooled liquid nitrogen **(215-001)**.

Organic Superconductors

ANL is involved in the design and synthesis of organic, organic/metallic, and inorganic compounds for organic electrically conducting and superconducting solids **(117-001)**. The current program objectives are to: (1) develop new derivatives of tetrathiafulvalene (a heterocyclic organic compound containing four sulfur atoms) that would provide organic solids with two-dimensional electronic structures **(391-007)**; and (2) develop new organic superconducting materials based on derivatized tetrathiafulvalenes and alkali-metal-doped C_{60} salts that have superconducting transition temperatures ranging from 1 to ~30 K. This research is supported by analytical capabilities **(391-009)** to measure the electrical transport of organic conductors (or other novel conducting materials) in the normal state and to determine T_c, critical magnetic fields and other properties of the superconducting state of these materials at temperatures below 300 K.

Biotechnology

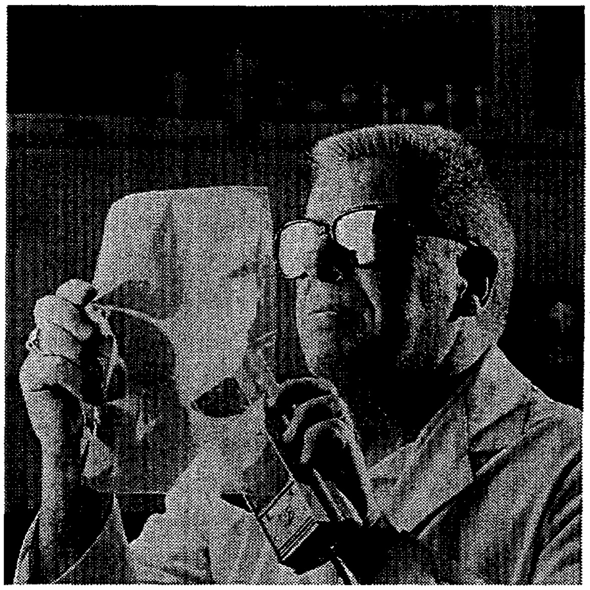

FIGURE 4 Degradable plastics made from starchy wastes **(642-002)**

Argonne has world-class facilities and expertise to support a wide variety of research activities in biotechnologies related to the chemical industry. Our ongoing biotechnology projects range from basic studies of biological phenomena to development of biocatalysts and bio-based processes for chemical production. Argonne, in collaboration with large and small companies, has developed or is currently developing efficient processes to integrate fermentation, product separation, and chemical conversion steps to produce chemicals from renewable carbohydrate feedstocks **(074-003, 074-001, 617-001, 642-002)**. These processes employ microorganisms — created or improved by using conventional and genetic metabolic engineering techniques — in highly productive bioreactor systems. We are also developing advanced membrane separation processes for fermentation product recovery. Novel polymer and specialty chemical products are synthesized by chemical conversion of the fermentation products.

Argonne's capabilities in industrial biotechnology applications are supported by our enormous resources in basic biological research. A database has been prepared containing published data on enzymes, microorganisms, and pathways that may be important for industrial chemical production. Robotics, 2-dimensional gel electrophoreses, and super-efficient biochips allow high-speed DNA sequencing and protein mapping of the primary industrial organisms **(077-003, 078-003)**. Argonne's Structural Biology Center uses the Advanced Photon Source (APS), which generates the world's brightest X-ray beams, to determine the atomic structures of proteins and other biological macromolecules. The APS will be a major tool in studying the use of chaperons to control protein folding and to improve enzyme stability **(078-007)**. High-performance computing facilities are used to analyze protein structures and functions and design improved enzyme catalysts **(052-002, 052-004)**. Protein engineering **(078-009)** is applied to enzymes to improve the substrate specificity, kinetic, stability, etc., of enzyme catalysts. We are also improving biocatalysts by using metabolic engineering of microorganisms to develop novel routes to chemical products and to increase the product yield, substrate range, and product concentration **(617-001)**. Enzymes that are stable in extreme physical and chemical environments are being isolated from archaebacteria that grow at temperatures around 100°C **(078-001)**.

Additional information on Argonne's biotechnology program can be found in the publication entitled *Argonne National Laboratory's Collaborative Approach to Advanced Biotechnology*. To obtain a copy of this publication, please contact Argonne's Information and Publishing Division at [630] 252-1632 or fax [630] 252-1393.

Catalysis

Catalyst studies at Argonne cover a very wide range of research interests: fundamental mechanistic studies, discovery of new catalysts and new analytical tools to characterize catalysts **(141-002)** and monitor catalyzed reactions, and development of novel catalyst disposal alternatives. Specialized user facilities such as the Advanced Photon Source **(078-020)**, the Intense Pulsed Neutron Source **(078-024)**, and the Transmission Electron Microscope represent another dimension of Argonne's catalytic capabilities. These projects and capabilities are described in greater detail in the *Catalysis Program Fact Sheets,* available from either Victor Maroni ([630] 252-4547) or Christopher Marshall ([630] 252-4310).

Argonne has been modeling catalytic reactions by using state-of-the-art quantum chemical techniques and developing unique ways to apply magnetic resonance imaging (MRI) to characterize catalysts. Computational chemistry, a tool that has not yet been widely applied in the area of catalysts, can be very useful to help guide experiments such as those involving hydrocarbon cracking in zeolites **(078-016)**. In a closely related area **(078-023)**, Argonne is using models of the interactions between metals and molecules to describe the dynamics of these interactions and to clarify how they work. MRI has provided fundamental data about fluid flow and reagent distributions within porous catalysts and through fluidized bed reactors. These techniques have also given scientists valuable insights into coking mechanisms **(078-011, 078-021)** and, for homogeneous catalysis, they have provided high-pressure data for carbonylation, hydrogenation, hydroformylation, and polymerization reactions **(078-015)**.

Several Argonne projects involve developing and testing new, high-performance catalysts for existing hydrocarbon processes **(079-009)**. For one such project, researchers are exploring new approaches for hydrodesulfurization catalysts **(078-012)**; the effort focuses on investigating nonclassical oxide supports, new active metal phases, and smaller metal cluster sizes. Argonne scientists are also investigating novel methods of synthesizing new porous supports for heterogeneous catalysts **(156-001, 180-001)** and characterizing a wide range of molecular sieve materials **(000-007, 078-019)**. The latter research includes studies on Fischer-Tropsch catalysis, methanol conversion, and methane activation. Another

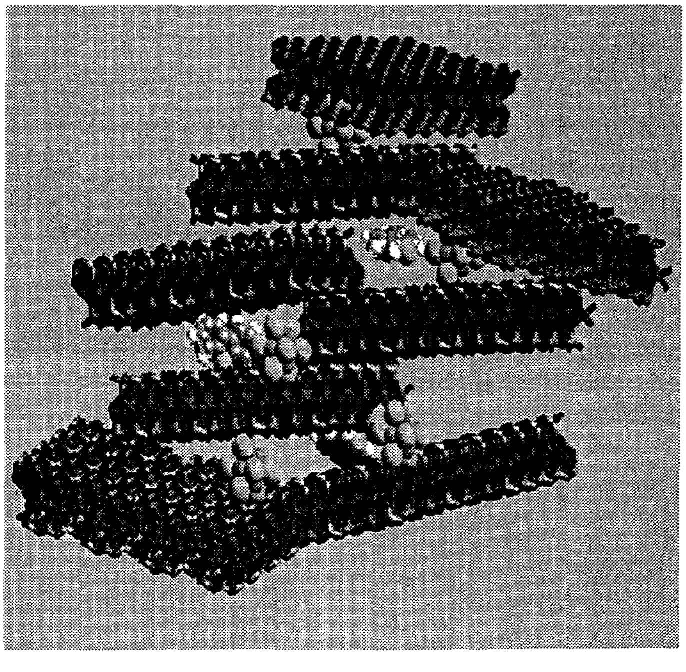

FIGURE 5 Metal cluster catalysts on modified clay supports are being developed for hydrodesulfurization (078-012)

project involves reforming alternate fuels for fuel cell powered vehicles **(700-002)**. Research into new processes includes one project to develop a photocatalyst that can recover heavy metal ions from aqueous solutions and convert them into less toxic metals **(151-001, 078-014)**. For another project, Argonne scientists are exploring a novel plasma-chemical process for producing and testing nanophase catalysts with significantly faster rates of reaction than current catalysts **(078-017)**. This process has produced very uniform metal particles with diameters ranging from 1 to 10 nm.

Materials

Argonne performs research on all classes of materials, including metals, ceramics, and organic-based materials. Materials-related research includes both basic investigations of structure/property relationships and development of practical engineering materials. Our materials research ranges from synthesizing novel materials tailored to specific applications to fabricating materials into practical components and evaluating their performance under actual operating conditions. Some of these research areas — ceramics, materials characterization, corrosion, failure analysis, metals, organics, radiation effects, and thin films — are described in the following sections.

Ceramics

Argonne's expertise in materials research includes the synthesis, fabrication, and characterization of a variety of ceramic materials: superconductors for the generation, storage, and distribution of energy; structural ceramics for high-temperature applications; phosphate-based materials for isolating radioactive and chemical waste; and electronic and ionic conductive materials used in electrochemical systems such as fuel cells and methane conversion reactors. Argonne has routinely used conventional fabrication techniques such as extrusion, tape casting, slip casting, and isostatic pressing, and we are now exploring the possibility of fabricating complex parts directly from three-dimensional computer models **(473-002, 656-001)**. Predictive correlations among structure, processing, properties, and performance of advanced engineering ceramic materials can be generated by computer simulations that are based on fundamental materials theory **(551-001)**.

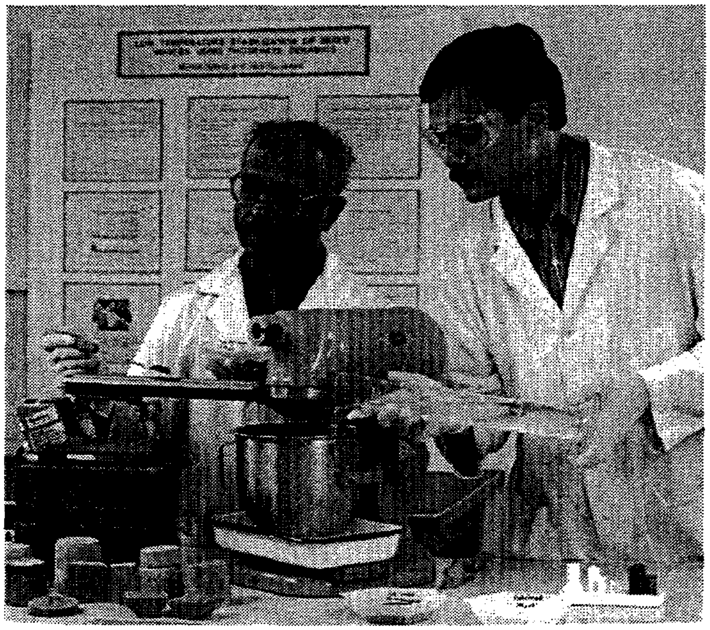

FIGURE 6 Ceramic technology effectively and economically handles hazardous wastes **(000-009)**

Argonne is developing phosphate-bonded materials as waste forms to solidify and stabilize mixed wastes that are not suitable for vitrification. The phosphate ceramic waste forms can stabilize wastes at room temperature so that no secondary waste streams are generated. Setting times are short, and the final waste form is leach-resistant, hard, and dense. The process is energy-efficient and economical and can be used to treat secondary waste streams produced by other thermal-treatment technologies. Initial tests indicate that these phosphate-bonded materials effectively stabilize wastes containing heavy metals regulated by the Resource Conservation and Recovery Act (RCRA); the tests also show that the materials have a compressive strength higher than that of portland cement. High-volume waste fly ash can also be bonded by phosphates and used in a pumpable slurry that sets in place to form insulator materials or strong structural ceramics such as bricks or precast panels. The process saves energy and time and stabilizes large volumes of coal combustion waste products **(000-009, 589-001, 590-001)**.

The Laboratory is equipped with state-of-the-art mechanical testing and microstructural evaluation facilities for structural ceramics, including continuous fiber ceramic composites. Researchers routinely evaluate mechanical properties (e.g., stress-strain relationship, first matrix cracking strain, ultimate strength, work of fracture, fiber/matrix interfacial strength) at room and elevated temperatures and have developed a special technique for evaluating in situ fiber strength in composites. These test procedures are applied to optimize processing and predict the reliability of ceramic composites used in high-temperature structural applications such as advanced heat engines, heat exchangers, and hot-gas filters **(495-001, 498-002)**.

Argonne has significant experience in synthesizing, fabricating, and improving the microstructure of ceramics for electrochemical applications such as fuel cells (e.g., molten carbonate and solid oxide fuel cells) and methane conversion reactors. Ceramic membranes developed at Argonne exhibit both electronic and ionic conductivity and promote hydrocarbon oxidation reactions without the need for electrodes. Such technology can be used to generate synthesis gas from the methane present in natural gas and offers significant energy and capital savings by eliminating the need for a cryogenic air separation plant **(495-003)**.

Materials Characterization

Argonne's extensive experience in materials characterization includes nuclear fuels and containment materials, engineered materials, and radioactive and hazardous waste **(056-001)**. Argonne researchers use a variety of techniques to evaluate these materials. Quantitative microstructural characterization employs optical and electron-beam microscopy and quantitative image analysis. Neutron and X-ray radiography and ultrasound, two nondestructive examination tools, are also routinely used. Computed tomography scan image reconstructions are produced from neutron and X-ray radiographs. We have also developed high-resolution, digital video systems for identifying and characterizing radioactive and hazardous waste materials **(213-005)**.

Argonne scientists use neutron and X-ray scattering methods to investigate the static and dynamic structure of crystalline and amorphous solids, liquids, polymers, surfaces, and thin films and determine the relationship between structural and physical properties. Current programs include studies of the structure and defect properties of high-temperature superconductors, magnetic surfaces and depth profiling of magnetic properties, the properties of polymers at surfaces and interfaces, and the structure of glasses and liquids **(010-008, 010-012)**.

Argonne's Electron Microscopy Center for Materials Research is an integrated research center with three major goals: (1) to further materials research by providing scientific and technical support and state-of-the-art instrumentation; (2) to conduct dynamic in situ studies of microstructural changes resulting from electron and ion irradiation, mechanical deformation, and gas/solid reactions in materials through direct observation by high-voltage electron microscopy; (3) to develop new and/or improved characterization techniques and instrumentation for high-spatial-resolution analytical electron microscopy. A battery of electron microscopes and an assortment of computers (Digital Equipment Corporation VAX 1 In85, five DEC PDP 11/23 class mini-computers, and a dozen microcomputers [IBM PC and Apple MacIntosh]) make up the core instruments of the center. A fully equipped specimen preparation laboratory and darkroom facilities are also available **(010-003)**.

Argonne uses directed energy sources (such as electrons, photons, and energetic ions) to modify and probe the surface composition and topography of a wide range of samples, including metals, oxides, microscopic grains, and polymers. The application of laser beam technologies to analyze surface impurities has achieved particular prominence; these procedures allow parts-per-trillion analysis in many cases. Secondary neutral mass spectrometry is used to probe the molecular and elemental distributions of surface and near-surface regions. These analyses can be performed with single monolayer depth resolution and sub-micron lateral resolution and can quantify concentration levels to below the parts-per-billion level. Maps showing chemical concentrations greater than 1 cm can be acquired using high-repetition desorption and photoionization lasers **(010-002, 398-001, 559-002)**. Pulsed ion beam surface analysis provides in situ characterization of thin-film deposition processes **(010-006, 010-007)**. Polymeric materials are analyzed using Fourier transform Raman spectroscopy, which is especially suited for on-line analysis of new and recycled plastics because little or no sample preparation is required **(124-001)**.

Our mechanical properties testing facility includes an Instron 8562 and an 8502 testing machine, each on a 250-kN load frame. The 8562 machine can perform conventional and very low-rate, long-time tests at temperatures up to 1650°C in a Centorr vacuum furnace. The 8502 machine is equipped with an environmental chamber ideal for testing elastomers in the stress relaxation and cyclic modes. The facility also has a fully equipped metallographic preparation area, scanning and optical electron microscopy instruments, and a heat-treating furnace with an inert gas purge system. Computer programs include databases for advanced energy system design and mechanical property modeling. Recent applications of the 8562 system include studies of the high-temperature mechanical behavior of structural stainless steels in relation to their microstructural evolution and measurements of the plastic flow behavior of the steels used in railroad rails to predict rail life. The 8502 system is currently being used to measure elastomer shear strength and energy dissipation capacity for seismic damping applications **(244-004)**.

Argonne has evaluated the thermodynamic and transport properties of a wide range of materials as part of the development of a nuclear materials database. The materials tested include uranium, plutonium, zirconium, aluminum, alkali metals, metal alloys, stainless steels, ceramic oxides, nitrides, and heavy water. An evaluation of the available data, including comparisons and assessments of experimental data and prior analytical work, has been used to compile the recommended values and uncertainties for these properties at temperatures from 298° to 6000° K. The results are available in both handbooks and databases **(429-003)**.

The Analytical Chemistry Laboratory (ACL) provides a broad range of support services. Phase analysis is performed via X-ray diffraction. Elemental and compositional analyses are usually conducted by using inductively-coupled plasma–atomic emission spectrometry (ICP-AES), although classical wet-chemical techniques (titrimetry, gravimetry) are applied when high-precision measurements are needed. Argonne has also established procedures for rapid, effective dissolution of most ceramics **(394-001)**.

Corrosion

Corrosion fatigue is a common degradation problem for components with high replacement costs and a long service life in power generation and fuel conversion systems. Argonne can predict the rate of degradation and the end-of-life properties of materials subjected to different environments **(529-001)**.

The Laboratory provides experimental data for testing theoretical models of the metal/water and metal oxide/water interface over a wide range of temperatures and in a variety of chemical environments. This research combines in situ surface-sensitive spectroscopic methods and interfacial electrochemical techniques with theory. Studies of microporous materials provide information on chemical reactions at the solid/liquid and solid/gas interfaces. These reactions are responsible for a wide range of phenomena that have both scientific and industrial significance: mechanisms of molecular-sieve crystal nucleation and growth, heterogeneous catalysis, gas-phase cluster formation, and chemical-vapor deposition of compounds and thermodynamically unstable crystalline phases **(010-001)**.

Argonne also evaluates the performance of materials in the simulated aqueous coolants present in nuclear reactors (boiling, pressurized, production, and fusion waters), in groundwater environments typical of intrusions into storage facilities for high-level nuclear waste, and in heat exchangers and thermal storage facilities for various energy conversion systems. The research addresses critical issues regarding the materials selection, reliability, and safety of high-cost, long-service-life components in these systems. Extensive autoclave facilities with slow strain rate tensile (SSRT) and cyclic crack growth rate testing systems are used in conducting corrosion and stress corrosion cracking studies of materials in high-temperature, high-pressure environments typical of those in which reactor coolants are found. Argonne tests irradiated materials by using an SSRT system located in a hot cell. On-line analytical instruments are used to monitor the electrochemical potential of the materials and the dissolved oxygen and impurity concentrations of the water in the refreshed, or once-through, systems **(532-002, 528-001)**.

Corrosion presents a major concern in the design of liquid metal cooling systems. Argonne is evaluating the corrosion and mechanical properties of structural materials in liquid metals (sodium, lithium, and gallium) at high temperatures. We are also working to develop stable corrosion-resistant electrical insulator coatings at the liquid-metal/structural-material interface, particularly coatings that prevent adverse magnetohydrodynamic- (MHD-) generated currents from passing through the structural walls. Experiments to synthesize intermetallic or ceramic coatings on candidate structural materials in liquid lithium are in progress **(524-001, 535-002)**.

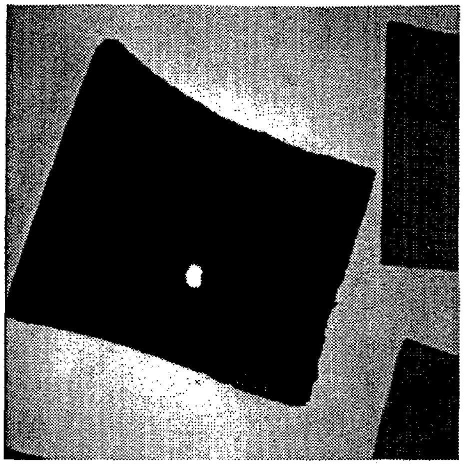

FIGURE 7 New control strategies for microbiologically influenced corrosion are being developed (526-002)

Bacterial colonies form deposits on metal surfaces and produce organic acids that accelerate corrosion and cause localized pitting. The bacteria act as environmental "catalysts," initiating a number of electrochemical and chemical corrosion processes. U.S. companies spend more than $200 million annually on water treatment chemicals to combat such microbiologically influenced corrosion (MIC). The total estimated cost of MIC to industry is $2 billion per year. Argonne and Southern California Gas Company have joined together, under a cooperative research and development agreement (CRADA), to develop more economical, environmentally benign methods for bacterial corrosion prevention than the biocide treatments now used by industry. This research effort **(526-002)** also includes screening and development of inexpensive MIC-resistant carbon steels and calibration and testing of on-line MIC detection methods.

We are currently evaluating the performance of metallic structural materials and corrosion-resistant coatings on alloys in gaseous environments that simulate conditions during power-generating processes fueled by coal. The complex gaseous environments include synthetic fuels (via gasification of coal), coal combustion environments (in bubbling and circulating fluidized beds), and combustion gases containing potassium salts (in MHD power generation systems). Our studies so far have focused on the corrosion/erosion behavior of low-alloy ferritic steels, austenitic stainless steels, nickel and cobalt base alloys, oxide dispersion-strengthened alloys, chromized and aluminized coatings, weld filler alloys, and weldments in high-temperature environments. Argonne has developed models that account for competing processes such as oxide scale thickening (via growth), thinning (via vaporization), and erosion (via particle impingement). The models enable researchers to identify the target areas for oxidation or erosion and predict the rate of metal consumption as a function of exposure **(526-003, 531-001)**.

The electrically insulating and corrosion-resistant coatings that are being developed by Argonne for use in magnetic fusion reactors have other potential applications. So far, we have developed and tested intermetallic AlN, TiN, MgO, BeO, and CaO coatings for steels and vanadium alloys. Development of garnet and/or spinel coatings will begin soon **(010-004, 294-002)**. Structural components made from porous MgO have also been developed for use in pyrochemical processing

Failure Analysis

Argonne has conducted fatigue and crack-growth-rate testing on a variety of structural alloys at temperatures ranging from room temperature to 800°C in air, in vacuums as low as 10^{-8} torr, and at temperatures as high as 300°C in pressurized water. Both cyclic fatigue and crack-growth-rate tests are conducted under axial loading conditions using closed-loop servo-hydraulic testing equipment; a wide range of loading frequencies and waveforms are possible. We can perform fatigue tests under strain, load, or displacement control and investigate elevated-temperature creep-fatigue interactions **(237-001)**. Monotonic tensile creep (stress-rupture) tests can be conducted on a wide variety of structural materials at temperatures up to 1100°C; test environments include air; inert gas; or several oxidizing, reducing, or sulfidizing gas mixtures formulated to simulate the required test environment. Axial extensometry and digital data acquisition instrumentation provide a record of the complete strain history of the test specimen during the test **(548-001)**.

Argonne's engineering mechanics staff predicted the response of 1:6-scale reinforced concrete (RC) containment vessels (including both two- and three-dimensional analyses of containment failure), completed post-test analysis of the RC containment, and discussed comparisons of the test data with our predictions. The Laboratory also analyzed full-sized containments for Soviet VVER reactor types. All the analyses were completed by using nonlinear finite element computer codes, in which the concrete and steel behavior are fully modeled. Concrete cracking was modeled through a smeared crack approach using a cracking criterion that is independent of element size to avoid size effects in modeling the structure **(237-004)**.

Argonne can perform heat conduction, elastic and elastic-plastic stress, and fracture mechanics analyses using either analytical, numerical, or finite element techniques. We have completed structural design and mechanical and thermal stress analyses to support the development of components for fusion reactor, fuel cell, and advanced battery systems. Life-prediction techniques developed by Argonne and design-life estimates computed for the metallic and ceramic components are based on fatigue and creep-fatigue crack initiation, crack propagation, and final fracture. The principal investigator for this project has been actively involved for the last 20 years in the American Society of Mechanical Engineers (ASME) Boiler and Pressure Vessels Code committees for high-temperature structural design; he belongs to an international team responsible for developing a design code for the International Thermonuclear Experimental Reactor **(238-001)**.

Argonne can conduct engineering mechanics analyses on various ceramic-fiber-reinforced ceramic/metallic matrix composites to predict residual stresses and stresses created by imposed loadings. Our techniques for convoluting the volumetric (not surface) distribution of residual stresses in composite materials are based on neutron diffraction data obtained at the Intense Pulsed Neutron Source here at the Laboratory and on validated predictions derived from engineering mechanics models **(238-001)**.

Argonne's failure analysis program involves the integrated efforts of a team of experienced researchers working to solve problems involving the deformation and fracture of materials. Our capabilities include the following: performing constitutive modeling on the basis of an understanding of deformation mechanisms and microstructure; applying these models to specific engineering problems through appropriate computer coding; and characterizing the mechanical properties, microstructure, and microstructural evolution of materials through experimentation. Our laboratory facilities, equipped with state-of-the-art mechanical testing equipment and microscopes, have been used recently to conduct high-temperature, low-rate experiments to support mechanistic modeling of the relationship between evolving microstructure and the deformation and fracture behavior of structural stainless steels, and to predict rail life by determining the mechanical properties of railroad steel **(534-004)**.

Cast stainless steels used in pump casings, valve bodies, piping, and other components in the coolant systems of light water nuclear reactors suffer a loss in toughness after many years of service at temperatures in the range of 290° to 320°C. Research is in progress to predict the ability of these components to withstand the loads imposed during normal operation, various postulated accidents, and severe earthquakes, because rupture of the primary system could lead to a loss of coolant **(538-001)**.

Metals

Argonne fabricates metals and composite materials by using a variety of processing techniques. Alloys can be produced by arc melting or induction melting in a vacuum or controlled atmosphere, and can be shaped by a variety of methods. Argonne's fabrication facility includes various sizes of rolling mills, draw benches, tubing reducers, welding equipment (including electron-beam), a 1/2-in.-capacity steel shear, swaging machines, straightening equipment, and hydraulic presses. Laboratory-sized extrusions can be produced, and furnaces measuring up to 24-in. by 24-in. by 72-in. and capable of reaching temperatures up to 2400°C (with controlled or vacuum atmospheres) are available for heat treating. The facility also includes an area for cleaning and chemical etching that is equipped with exhaust systems, specialty equipment such as a hot isostatic press and a high-energy impact mill, and complete metallographic facilities to study the microstructure of the materials processed **(532-001)**.

The Laboratory also performs computer calculations of thermodynamically consistent and optimized phase diagrams for binary and ternary alloys. Existing phase diagrams can be assessed for reliability, and unknown diagrams can be calculated with minimal experimental information **(491-001)**.

Organics

Argonne employs a number of groups that specialize in the design, synthesis, and complete characterization of novel organic materials, with a special emphasis on optical materials, photochemical systems for solar energy conversion, and materials with novel electronic and magnetic properties for advanced electronic components, sensors, etc. By establishing structure/property relationships in these compounds, the groups develop strategies for synthesizing environmentally safe, lightweight organic materials with the desired physical properties. The groups have facilities to completely characterize new materials — they have designed and prepared well over 1,000 new materials in the past several years **(123-002)**.

Several groups focus on the development of conductive and superconductive organic compounds with electrical conductivity that arises solely from nonmetallic organic molecules rather than metal atoms. This research program has resulted in extensive capabilities in synthesis and characterization of organic materials, including significant expertise in single crystal preparation. The program is also supported by a theoretical modeling effort **(090-001)** to characterize the large-scale electronic structure of these materials.

The Laboratory is equipped to conduct thermal reactions (ambient to 1,500°C), ultrasonic reactions, pressure reactions, and electrochemical synthesis. Special techniques include handling of air-sensitive materials, use of inert atmospheric dry box and Schlenk techniques, and vacuum line operation (10^{-6} torr). Separation and purification techniques practiced at Argonne include column chromatography (thin-layer, gas, and liquid), crystallization and electrocrystallization, and sublimation with carrier gas (under vacuum or gradient conditions). Characterization techniques include ultraviolet-visible; Fourier-transform infrared (FTIR) spectroscopy; nuclear magnetic resonance (NMR); electron spin resonance (ESR) spectrometry for free radical detection; Raman imaging microscope spectrometry for semiconductors, polymers, ceramics, etc. **(010-009, 391-005, 391-006, 391-007)**; and X-ray diffraction for crystal structure determination, both at room temperature and at cryogenic temperatures. Several single-crystal X-ray diffractometers, some with low-temperature (as low as ~15 K) capabilities, a powder X-ray diffractometer, and several film X-ray diffraction units, as well as necessary computer support, are available for characterization efforts **(387-001)**.

Radiation Effects

Materials are often subjected to environmental conditions that produce changes in their microstructure and microchemistry after extended service. For example, major components in nuclear and fossil fuel power plants can become brittle, and their useful service life can be reduced because of thermal aging and/or fast neutron irradiation. Argonne has a well-established reputation for remote handling, characterization, and testing of radioactive materials and for investigating the influence of irradiation on the microstructure and physical/mechanical properties of materials (structural materials, oxide- and/or graphite-based nuclear fuels, silica, low-Z oxides, and organic-ceramic composites) in a variety of environments. For example, materials scientists at Argonne extensively use Auger electron spectroscopy **(379-001)** to quantify changes in the grain boundary microchemistry of austenitic stainless steel specimens obtained from light-water reactors. They probe the mechanisms of radiation damage in insulator materials such as amorphous silica and other low-Z oxide materials (used as insulators and optical waveguides in the semiconductor and communications industries, and considered as possible future sensors and radiation detectors). The goal of this work is to understand the mechanisms that degrade component performance and, where possible, protect against the damage and/or propose materials that have greater resistance to degradation **(209-001, 546-001, 095-001)**.

Thin Films

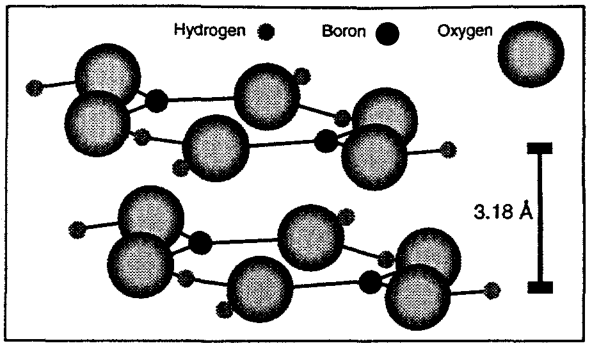

FIGURE 8 Boric acid films decrease friction and wear **(581-001)**

ANL has expertise in preparing and testing coatings **(510-001, 579-001, 678-001)** that provide improved friction and wear properties for use on engine surfaces and in low-emission, high-fuel-efficiency transportation systems. The coatings can be made from a variety of materials (including boric acid **(581-001)**, lubricious oxides, soft metallic films, diamond and diamond-like carbon [DLC] films). Argonne scientists can deposit the complex thin films by an assortment of techniques (microwave plasma-assisted chemical vapor deposition [CVD] and plasma sputter deposition) and characterize their growth in situ, resulting in new tools for understanding the mechanisms of thin film growth and for controlling fabrication of thin film devices.

Ion beam-assisted deposition combines conventional physical vapor deposition with ion bombardment to deposit coatings of any material that can be evaporated by conventional means. The chemical composition and microstructural properties of the films can be tailored by controlling the evaporation rates, the partial pressure of reactive gases (e.g., oxygen, nitrogen, or methane), and the energy and current density of the ions bombarding the substrate/film during deposition **(010-006, 513-001)** or by laser heat treating **(015-003)**.

Argonne can prepare ultrathin metallic films in novel epitaxial overlayer, sandwich, and superlattice configurations to atomically engineer magnetic, semiconducting, superconducting, elastic, and optical properties of interest and to utilize new techniques for characterizing structure/property relationships. Current studies focus on magnetic coupled-layer phenomena, growth, morphology, phase stability, anisotropy, critical behavior, transport, dimensionality, and supermodulus effects **(010-007)**.

DLC is a form of amorphous carbon that is many times harder than steel, resists wear, offers low friction when sliding against many materials, and is extraordinarily inert. DLC coatings can be produced on materials at room temperature, eliminating the risk of damage to heat-sensitive parts **(509-001, 509-003, 511-001)**. Thin diamond films can be grown on a variety of materials by using microwave-enhanced CVD. Varying the processing conditions allows researchers to tailor smooth or rough diamond films **(511-001)**. Computer programs developed at Argonne for fusion-device simulations reveal a potential for predicting the transport of material to and from a surface exposed to magnetized plasmas; these programs may prove valuable in developing plasma-assisted CVD processes **(518-001)**.

Growth of the coatings can be monitored in situ during deposition **(509-001)**. In addition, friction and wear tests of the coatings can be performed over a wide range of temperatures, pressures, and speeds **(578-001)**. Argonne uses a variety of techniques to characterize thin films:

microhardness measurements, profilometry, Auger electron spectrometry, energy dispersive analysis by X-ray wave length dispersion spectrometry, adhesion strength measurements, scanning electron microscopy, transmission electron microscopy, and FTIR and Raman spectroscopic interface studies **(523-001)**.

Environmental Chemistry

For over 25 years, Argonne has been a leader in developing and evaluating environmental technologies in energy and other industries. The Laboratory conducts basic and applied environmental research, development, and assessment projects in support of the U.S. Department of Energy and other public agencies. These projects range from site-specific assessments to global climate change studies and encompass a wide range of disciplines, including the Laboratory's core capabilities in the basic sciences — physics, chemistry, and biology — and advanced evaluation methods to analyze specific environmental problems and policies. Specific examples of these diverse projects are summarized in a two-volume brochure — *Environmental Restoration and Waste Management* (Vol. I) and *Environmental Research, Technology, and Assessment* (Vol. II). The purpose of this summary of Argonne capabilities is to focus attention on those projects of greatest interest to the chemical industry. For more information about projects from these other areas, please contact Argonne's Office of Environmental Sciences ([630] 252-3759).

FIGURE 9 Bioremediation cleans wastewater (**074-002**)

Since those environmental brochures were prepared, Argonne has begun several new environmental programs of interest to the chemical industry. Among these is an effort to develop disposal technologies for waste streams containing hazardous metals, including plating waste and industrial waste water **(201-001)**. This process involves alkaline sulfide precipitation of hazardous metals and their subsequent removal by filtration to produce a nonhazardous liquid for disposal. Another program involves evaluating a gas treatment and purification system that can be installed on incinerators and vitrification processes to virtually eliminate hazardous releases to the environment **(201-006)**. This research employs a 250,000-Btu/h (75-kW thermal) combustor to demonstrate removal of combustion product CO_2 in a fluidized bed of CaO (lime) and collection of particulates in hot-gas candle filters. For another project **(553-001)**, Argonne scientists are evaluating the long-term stability of different disposal technologies over a range of possible disposal conditions. Argonne is also exploring the use of phosphate-bonded materials as waste forms to solidify and stabilize hazardous wastes that are not suitable for vitrification (conversion into glass or a glassy substance by heat or fusion) **(000-009)**. This approach uses the phosphate ion as an inorganic binder for waste solidification; this ion stabilizes heavy metal contaminants by exploiting the very low solubilities of the heavy metal phosphates.

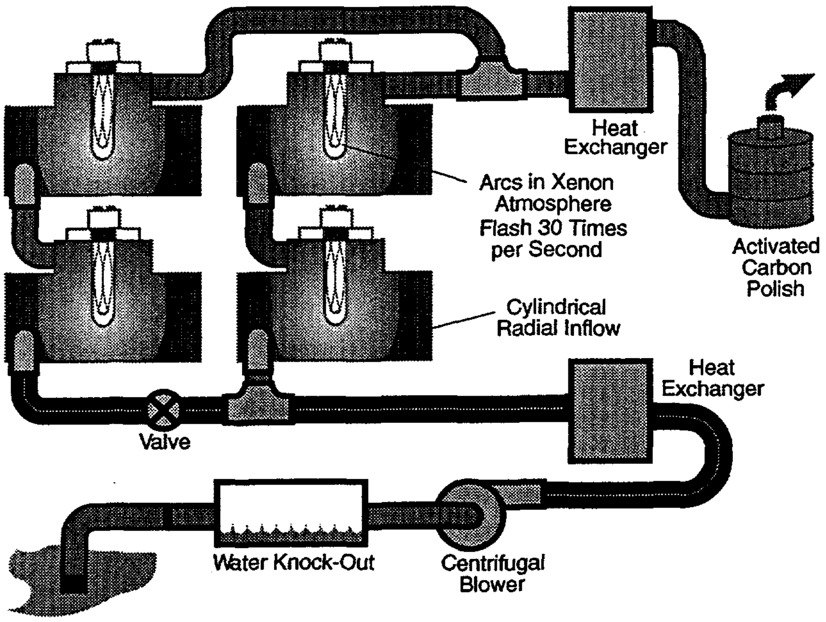

FIGURE 10 Ultraviolet radiation destroys contaminants (601-002)

Other Argonne projects have targeted specific industrial wastes. In one program, Argonne scientists are using novel molten sodium technology to destroy halogenated and other toxic organics **(448-002)**. The objective of this project is to generate design data for a system to treat toxic organics for the waste management industry. Another project is testing ultrasonic technlolgy for detoxifying contaminated soils and groundwaters **(585-003)**. A third project involves developing a bench-scale unit to validate a modified plasma-hearth process that will vitrify hazardous materials **(611-003)**, and a fourth employs a microwave-generated plasma to dispose of hydrogen sulfide **(599-002)**. The latter approach has the added advantage of producing a valuable chemical reagent — hydrogen.

Petrochemistry

Argonne is conducting several research projects to address petroleum refining issues that may interest the chemical industry. These projects include basic research in catalysis (see Catalysis section) and in chemical thermodynamics of high-molecular-weight hydrocarbons (see Chemical Research section). Argonne has extensive experience in computational fluid dynamic modeling of multiphase unit operations (such as fluid-bed reactors), which is being applied to developing advanced catalytic cracking technology (see the Advanced Process Design and Analysis section). Other projects include the development of new analytical techniques and sensors for on-line process monitoring/control (discussed in the Analytical Chemistry and Sensors sections), evaluation of novel environmental control technologies for liquid discharge/waste water, and development of industrial site characterization and remediation technologies (covered in the Environmental Chemistry section).

Argonne is participating with the refining industry in several cost-share projects on heavy oil and residual oil processing. One area of research involves characterizing asphaltene using advanced techniques and batch evaluations of hydroprocessing catalysts **(173-001, 174-001)**. For these evaluations Argonne scientists use in-situ methods to follow the hydroprocessing chemistry at reaction pressures and temperatures and to directly determine the decrease in asphaltene size by small-angle neutron scattering. Closely related projects involving coal chemistry include the following: structural and chemical studies of coal samples, petroleum resids, and heavy crudes **(154-001)**; characterization of the structure and reactivities of coal materials **(161-001)**; and maintenance of the Argonne Premium Coal Samples Bank **(161-002)**. Projects addressing heat transfer research are discussed in the Heat Transfer section.

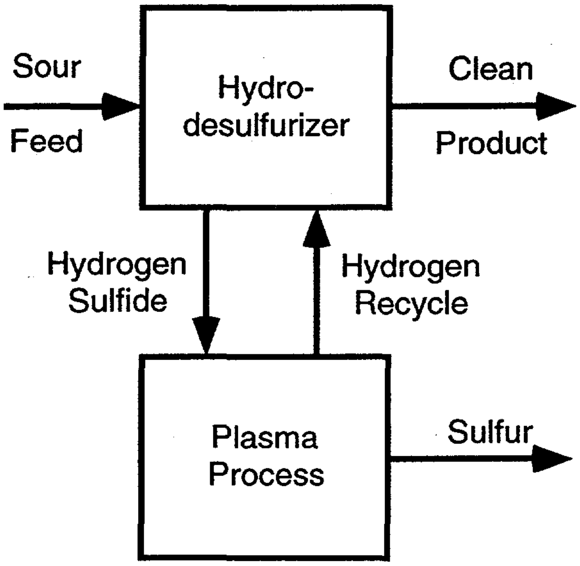

FIGURE 11 Plasma-chemical process recovers hydrogen chemical value from hydrogen sulfide **(599-002)**

The projects discussed above involve improving existing processes; Argonne is also developing novel process technologies to make more efficient use of hydrocarbon resources and for resource recovery and recycle. The former objective applies to a project in which researchers are studying the direct, partial oxidation of methane to syngas with a ceramic membrane reactor **(495-003)**. The key to this technology is a dense ceramic membrane that allows air to be used instead of oxygen. For another project, Argonne researchers are using a plasma-chemical reactor to split waste hydrogen sulfide into hydrogen plus sulfur **(599-002)**. This process uses microwave energy to drive the thermochemical reactions and recover the hydrogen reagent value contained in this industrial waste stream. A preliminary engineering assessment demonstrates the technical feasibility and economic competitiveness of the process.

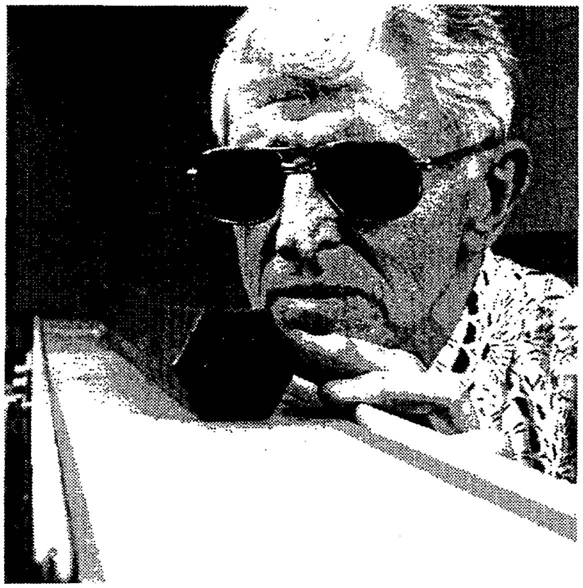

FIGURE 12 Ceramic-membrane reactor produces syngas from methane and air (495-005)

Unit Operations and Automation and Information Systems

Advanced Process Design and Analysis

Argonne has developed and tested state-of-the-art computer codes for a wide range of unit operations. In the following paragraphs, we describe many of these programs that could be used to model chemical processes. Other programs that address process safety issues are described in the Safety section.

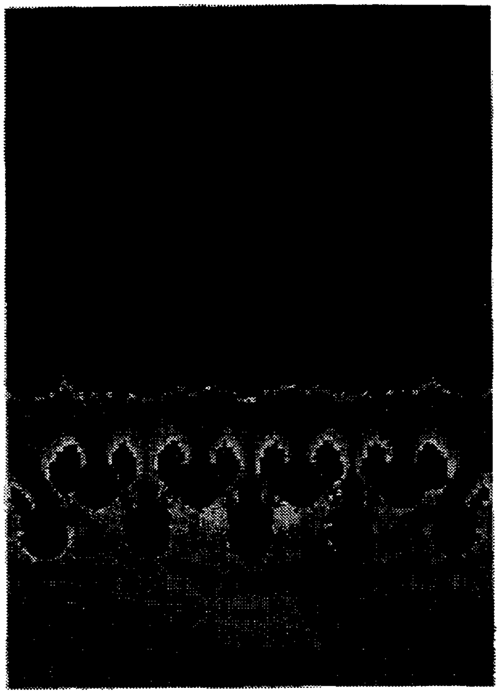

FIGURE 13 Fluidized bed simulation **(078-022)**

The Laboratory has developed a computer code named FLUFIX to predict hydrodynamics in complex fluidized-bed reactor (FBR) and fluidized-bed combustor (FBC) systems. This code is based on a hydrodynamic model of fluidization and can predict the frequency of bubble formation, bubble size and growth, bubble frequency and rise velocity, solids volume fraction, and gas and solids velocities for both atmospheric and pressurized bubbling and circulating FBRs and FBCs. The results of the hydrodynamic model are used as input to ANL's EROSION/MOD1 computer program, which contains various erosion models, including our unique monolayer energy dissipation erosion model. Argonne has also developed the FORCE2 computer code, a three-dimensional transient and steady-state version of FLUFIX/MOD2. We have implemented the FLUFIX and FORCE2 computer programs on the Laboratory's CRAY-XMP vector supercomputer and IBM RS/6000 high-end workstations and performed quality assurance and validation. FLUFIX/MOD2 is being extended to model fine-powder fluidization in a collaborative project with Dow Corning Corporation and Fluent, Inc. When completed, the new program will be able to predict the rheology of fine powders from the fixed-bed state to pneumatic conveying — including cohesive and Van der Waals forces and solids stress-strain relationships.

Argonne has developed a general, multiphase, non-Newtonian, hydrodynamic model to predict spatial and temporal distributions of pressure, relative motion, concentration and mixture shear rate, and viscosity for slurry flows (SLUCAL/MOD1). This model includes separate continuity and momentum equations for each phase and extends the non-Newtonian constitutive relationship for power-law mixture shear stress **(219-002)**. Recently the COMMIX-M program was enhanced to account for turbulence enhancement and suppression caused by particulates. The approach is based upon extending Reynolds Stress models of turbulence by including appropriate sources and sinks.

Argonne researchers have generated many unique ideas for improving industrial processes to minimize waste and save energy. From these numerous new alternatives, a few promising ones must be selected before initiating costly experimental testing or constructing pilot-scale facilities. Argonne uses the latest, most accurate computer software to mathematically model a concept, such as recovering valuable hydrocarbon liquids or polymers from the shredded residue of junked automobiles or refrigerators. Argonne uses such sophisticated programs as ASPEN PLUS (for chemical and thermal processes), METSIM (for metallurgical processes), and HSC Chemistry and FACT (for calculating chemical reaction equilibriums). These commercially available models save time and money while providing a rigorous mathematical framework for comparing alternatives **(639-002)**.

Argonne has developed a two-phase, solid/gas flow model that describes the flow inside a variable-area duct. The model includes multiparticle equations and considers particle/particle interaction. The predictions made by the model compare favorably with experimental data. The code can be used to design an instrument for measuring the solid flow rate in solid/gas flow processes **(283-001)**.

Another Argonne computer code, ALICE (Arbitrary Lagrangian Implicit Continuous-Fluid Eulerian), can analyze fluid transients, pressure differentials, and structural responses in fluid-filled cylindrical shells (with internals) under abnormal conditions, such as those generated from chemical and nuclear reactions and internal explosions. The code is a fast running, user-friendly computer program that uses hybrid Eulerian Lagrangian meshes and treats accurately extended fluid motions and large structural displacements. The computer code has been validated extensively and could have safety-related applications in the chemical, nuclear, petroleum, and waste management industries **(708-001)**.

The SWAAM-II code was developed to analyze the pressure effects of sodium/water reactions in a liquid-metal reactor steam generator system. The SWAAM-II model is generally applicable in situations where gas is suddenly generated or released into the bulk liquid environment of an industrial process system. The model enables scientists to assess the resulting overpressures and coupled pressure propagation throughout the system. SWAAM-II has been used to analyze a fission gas release in the fuel pin bundle of a reactor core. The model was developed as a general-purpose code applicable to any complex system geometry, including piping networks. No other similar model or computer code is currently available **(287-002)**.

The Generic TRUEX Model (GTM) was first developed as a tool to design flowsheets for TRUEX solvent extraction, which is a process to remove and recover transuranic elements from highly acidic aqueous solutions during reprocessing of irradiated fuel. The GTM has several key features that expand its usefulness beyond this initial application. These include the ability to calculate the following: (1) mass balances for multistage (256) countercurrent flowsheets with up to 25 feed streams (including rerouting of section effluents) in a variety of contacting equipment; (2) the complex aqueous-phase speciation, thermodynamic activities, solubilities, and extraction behaviors in highly complex solutions containing a variety of cations and anions, and (3) the space and cost associated with installing a solvent extraction process. This user-friendly model was written using Microsoft Excel so that new features can be easily added; for example, other anions and cations and new aqueous-phase complexation equilibria to the speciation calculations or new unit operations to the space and cost calculations. We are looking at opportunities to expand our expertise in modeling chemical processes into new areas **(094-001)**.

Expert systems based on fuzzy logic are being used at Argonne to monitor complex industrial processes to determine whether the process variables are within acceptable tolerances. If not, the expert system pinpoints the cause of the problem, identifies the fault, and prescribes corrective actions **(354-001)**.

Complex systems are modeled using the data obtained from either direct measurements of an operating system or from a mathematical simulation of the system using neural networks. These networks, once trained, are much less complex than the first principles models. If the first principles models cannot be obtained (e.g., because of a lack of understanding of physical and/or chemical processes), neural network models may provide the only alternate method of describing the system. Neural networks can be applied to system control, optimization, monitoring, fault detection, and diagnostics **(335-001)**.

The ICRKFLO model is used for detailed internal process analysis of individual flow system components. Such analysis may uncover problems in individual components or improve the performance of those components. This ability can be critical to the overall operation of the entire system. The analysis may concentrate on component efficiency or operational lifetime (which can be limited by fouling, erosion, etc.) or on minimizing pollutants. ICRKFLO has been successfully applied to the analysis of coal-fired combustors in MHD power generation, air-breathing jet engines with fuel spray injection, diesel engines, particle-laden nozzle flow, and seed particle injection in the deswirl section of an MHD power train. Finally, the model is being applied to three-phase reacting flow in a fluid catalytic cracker riser to help develop technologies used to process heavy residual oil into useful fuels or other petroleum products. The code has been verified by comparison with experimental results for several applications. The computer code is operational on a CRAY supercomputer, a VAX minicomputer, or an IBM-compatible personal computer (486 or better). The model may be used for either steady or unsteady flow computations; both two- and three-dimensional versions are available **(282-002)**.

Argonne's SALT system simulation computer code is a systems-analysis and process-simulation computer code for steady-state and dynamic systems. It has been used to evaluate the performance of various energy and flow systems through sensitivity and optimization studies. Based on a preprocessor concept, the SALT code uses a language translator to allow the user great flexibility in specifying a systems-analysis problem. Submodels for many energy system components, such as combustor, steam turbine, heat exchanger, pump, compressor, steam drum, condenser, and stack (for general description of energy and flow systems), have been developed and are included in the code. The model also includes thermodynamic and transport property routines that can be readily reconfigured into various applications for energy and flow systems **(227-001)**.

Planners, regulators, and the public can more clearly understand how a proposed construction project can affect the environment if they can "see" how it relates spatially to its surroundings. Visualizations of potential projects can communicate complex spatial information more vividly. Innovative techniques developed and/or applied at Argonne help users to visualize spatial data produced by computerized systems. Nontechnical audiences can interpret these data by viewing perceptual devices or geographic information system (GIS) and computer-aided design images linked to scanned photographs and maps **(057-002)**.

Argonne researchers are working on methods and devices to mitigate pressure pulses that may occur in piping systems and components. One of the methods is based on accelerating high-pressure fluids through a device perforated with small openings, thereby transforming harmful pressure energy into kinetic energy and a small amount of heat. Argonne developed test models to demonstrate the performance of this technology. The method is simple, reliable, and economical and offers great potential commercial value. It can be applied in situations where large pressure surges must be controlled or to mitigate relatively small surges (such as in some control systems); it may be used in chemical or other hostile environments. A U.S. patent for the technology has been issued **(288-001)**.

Analytical models and computer codes have been developed to analyze transient flows in complex piping networks. The PTA-2 code addresses water hammer using the characteristics method. In addition to its capacity to analyze general piping flow, the PTA 2 code incorporates fluid/structure interaction effects for deformation and cavitation of plastic piping by column separation. The code has been extensively validated against experimental data. The SWAAM-LT code offers the computational capability for quasi-steady incompressible flows in a piping network. A module of SWAAM-II models transient compressible single- or two-phase flows, combining finite-difference and characteristics methods. Many of the capabilities of these codes are unique; they are not available in commercial software **(287-003)**.

The design and optimization of complex systems are complicated by the numerous possible interactions between the system's components and the difficulty in determining the best set of system parameters to satisfy design requirements. The problem is compounded for dynamic systems because the interactions constantly change with time. Our expertise and methodologies in design and analysis of advanced power and propulsion systems for DOE, the Air Force, and NASA have led Argonne to develop a flexible computer-based framework for modeling complex systems that consist of arbitrary components interconnected by information flows. Constraints and optimization conditions may be applied over the system variables. Many thousands of these conditions can be efficiently handled to model realistic systems with many degrees of freedom. A graphical user interface provides point-and-click control of the simulation on a workstation, and dynamic two- and three-dimensional plots allow the user to visualize the simulation results. Argonne can also devise and link realistic visual interfaces to the simulations to provide an accurate visual representation and interaction with modeled prototypes. This capability has been applied to advanced energy, propulsion, and manufacturing systems **(319-001)** and to the control of such systems **(295-002, 331-001)**.

Safety

Argonne has extensive experience and state-of-the-art analytical tools and experimental facilities for conducting deterministic and probabilistic safety analyses and related experimental work. In deterministic analyses, systems and facilities are analyzed to assure that their design satisfies safety requirements. In probabilistic analyses, researchers evaluate qualitative and quantitative hazards and risks to improve systems design and operations and demonstrate compliance with regulatory requirements.

Our state-of-the-art computer codes are used to perform fluid flow and heat transfer analyses under transient and accident conditions **(300-002)**. These codes cover all modes of heat transfer (conduction, convection, and radiation), laminar and turbulent flows, single and multiphase flow and heat transfer, and analyses at the system- as well as the whole-plant level. Argonne's experimental facilities are used to validate computer codes and systems analyses and to help understand complex phenomena under transient and accident conditions (e.g., reactive and explosive interactions) **(290-001, 312-001, 267-001)**.

Argonne also conducts analyses of fluid transients and mitigation of associated pressure pulses; we have developed computer models to treat both short-term and long-term transients in complex piping and heat transport systems **(235-002, 236-002, 236-003, 241-001, 285-001, 287-001, 287-002, 287-003)**. Phenomena analyzed here at the Laboratory include cavitation, elastic-plastic pipe deformation, fluid-structure interaction, interface treatment and pipe filling, multidimensional flow regions, and interaction of gas or chemical reaction bubbles with the fluid system. The models are extensively validated against experimental data and are applied to a variety of safety and fluid system design problems. Laboratory experiments and analyses have led to the development of pressure pulse attenuation methods and devices; one of these devices has been patented.

We develop models and analyze problems of rapid decompression of pressure vessels and piping and pressurization of compartments **(282-001)**. The modeling for both cases may involve compressible gas flows or two-phase flows. The latter can be modeled by using an approximate analytical formulation or by more exact representations of the equation of state for the fluid. Researchers here at Argonne have developed a computer code that employs a unique hybrid computational method to calculate piping system depressurization or pressure transients in such systems. Other computational approaches were developed to study the pressure rise in compartments subjected to high-pressure fluid inflow. These methods have been successfully used to analyze transient phenomena in a number of nuclear reactor and industrial applications, and are directly applicable to many transient flow and accident situations that may arise in the chemical and petroleum industry (e.g., high-pressure pipe or vessel rupture, valve failures, high-pressure fluid discharges into confined spaces).

Scientists at the Laboratory have also developed advanced fluid-structure interaction computer codes to simulate the behavior of fluid-structure systems to internal and external

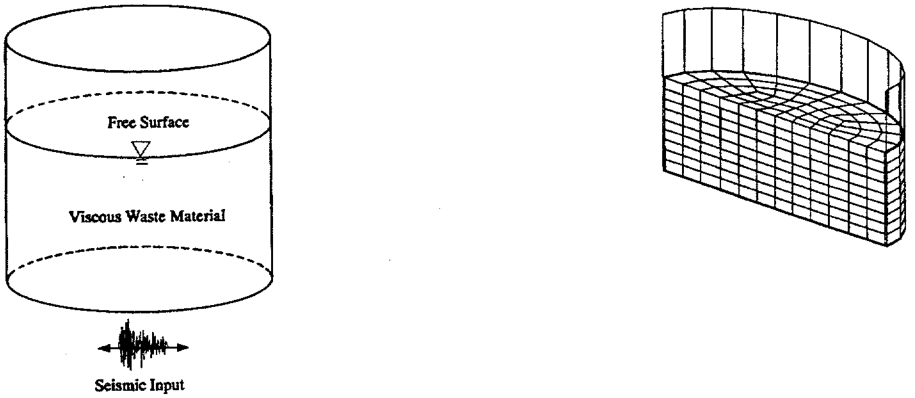

FIGURE 14 Simulating the seismic behavior of storage tanks (**286-001**)

transient loadings **(236-001, 309-001, 013-001, 311-001, 239-001, 239-003)**. Cylindrical vessels containing fluids, fluid-filled cylindrical vessels embedded in a fluid-filled well, and piping systems can be analyzed for transient response. An advanced three-dimensional computer code can simulate the sloshing response of vessels containing several layers of fluids to earthquake ground motions. We have also developed methods for vibration and acoustic monitoring of vessels and piping systems.

Argonne's experience in reliability and safety analyses includes the following qualitative analyses: preliminary hazards analysis, "what if" analysis, hazop, failure modes and effects analysis, and sophisticated state-of-the-art quantitative probabilistic safety analyses (PSAs) **(353-002, 367-002, 367-003, 533-001, 213-002)**. In PSA, researchers use fault trees and event trees to quantify system unavailabilities and the frequency of accident sequences. Then, the effects of accidental releases of hazardous materials on population and the environment are assessed in terms of frequencies of occurrence and magnitude (e.g., frequency of more than N illnesses per year).

In operating plants, the information generated from PSA analyses is used to redesign plant components or systems; redesign or improve the man-machine interface; and improve maintenance and operating procedures, emergency procedures, spare parts and maintenance policies, operator training, and plant availability. These changes enhance plant safety and reduce operating costs and the investment risk from accidents that compromises the integrity of the plant.

In designing advanced power plants, Argonne has used the probabilistic safety assessment methodology as an integral part of its plant design method **(213-006, 213-007)**. This method assures that the new plant meets pre-set risk and availability goals and eliminates the need for costly backfits over the life of the plant.

Separations

Separations are an integral and critical part of chemical processes. They are used in all processes to recover products and remove contaminants — gases, liquids, or solids. Increasingly more stringent environmental regulations have placed new demands on separation technology. Novel, more selective, and more efficient methods are needed in all aspects of separations technology.

Argonne has many ongoing programs covering a broad spectrum of both applied separation science and fundamental work on innovative separation methods. Much of this work is interdisciplinary and encompasses groups with a wide range of expertise.

Solids Separations

Separation of solids requires a broad range of expertise in many fields. Some of this expertise involves only a fundamental familiarity with a system; some involves a broader scientific understanding of the nature of particles in different media. Solid separations require a thorough knowledge of variables such as particles size, surface properties, and particle heterogeneity, which are not always easy to understand in real-world processes. Argonne is involved in a number of projects in solids separation — from very large, centimeter-size particles to submicron materials.

The Laboratory is testing a potentially economical procedure to separate and recycle heat-formed plastics (thermoplastics), polyurethane foam, and iron-rich "fines" from waste that remains after metals are recovered from scrapped automobiles. The foam and fines are removed mechanically. The foam can be used to manufacture carpet padding, while the fines are used in the cement industry. A chemical process is used to dissolve and recover the thermoplastics. Argonne is developing similar low-cost technologies to reclaim and reprocess the plastics from discarded appliances **(201-007, 642-001)** while a closely related project is studying the recycling of waste lubricating oils.

In the area of gas/solid separations, Argonne is involved in a variety of projects to evaluate existing particle control methods and develop new technologies. Recent programs include quantifying the capture efficiencies and massloading characteristics of prefilters and high-efficiency particulate air (HEPA) filters, devising methods to measure and extend the useful life of high-temperature ceramic filters that are subjected to cold cleaning pulses, and developing a heavy metal vapor removal technique based on condensation and thermophoretic deposition **(585-001)**.

We are also developing techniques to separate materials using their magnetic properties. The Open Gradient Magnetic Separator (OGMS) is an extension of Argonne's widely recognized expertise in the development of superconducting magnets. The OGMS is used to separate metal-contaminated solids such as catalysts in order to improve their performance and to decrease the waste disposal stream. Working with Bradtec, Inc., Argonne personnel are developing the basic technology and applications for specially designed magnetic particles that can remove dyes and chemicals from process or waste streams **(315-001).**

Separation of ultrafine particles presents an enormous problem for industry. Fine materials cause many pollution problems and often require energy-intensive methods to remove. Many processes are limited by the amount of fines they generate that require treatment. Argonne is involved in several programs that address the issue of fine particles.

Researchers are developing aqueous biphasic separation (ABS) systems for processing ultra-fine particles in the micron and submicron size range. The ABS partitioning systems are generated from combinations of water-soluble polymers and inorganic salts. The separation technique relies on subtle differences in particle surface chemistry to control selective partitioning of the particles between the two immiscible aqueous phases **(201-003).**

ANL has significant experience in the development of sedimentation methods both for separating and characterizing ultrafine fossil fuel materials. Our recent work has focused on characterizing solid catalysts. The aim of this fundamental work has been to develop separation methods that can be used to monitor and study the chemical and physical variability of particulate systems. Both simple and sophisticated methods of determining density, including sink/float centrifugation, continuous flow centrifugation, and density gradient techniques, have been successfully applied to fine and ultrafine particle systems. Fine grinding techniques and control of particle aggregation through particle surface modification are also important aspects of this work **(160-001).**

Liquids (Extraction and Soluble Species Removal)

Argonne has a particularly long and productive history in the area of extractions and in liquid/liquid separations involving the selective concentration or removal of ions from liquid phases. This expertise comes from many long-standing, active programs in nuclear fuel reprocessing. However, an increasing portion our work is now directed toward non-nuclear environmental cleanup.

One active program involves the development and demonstration of solvent extraction flowsheets. Work is currently underway to collect batch-contact data and perform countercurrent, multistage demonstrations of partial and full flow sheets for the TRUEX, TRUEX/SREX, and NEPEX processes. These processes are mentioned because (1) they perform different separations; (2) they are currently being evaluated for different DOE waste treatment needs; (3) their solvents have different compositions, densities, and dispersion characteristics; and (4) their flowsheets are significantly different. Separations tests using natural isotopes and radiotracers are being conducted in a 20- to 24-stage centrifugal contactor **(201-002).** This research also involves developing resins for waste management and water purification **(205-002).**

This centrifugal contactor for multistage solvent extraction processes was developed entirely at Argonne. Contactors with throughputs from 0.04 to 120 L/min have been successfully designed, built, and used in DOE facilities at Argonne, Oak Ridge, Savannah River, Hanford, and Los Alamos national laboratories. Key contactor features include a simple design, ease of use, compact size for a given throughput, low liquid holdup for fast startup and shutdown, reliability, ease of maintenance, well-defined stages with high extraction efficiency, and easy access to each process **(443-001)**.

Groundwater contaminated with heavy metals presents a concern at several DOE and industrial sites. We are investigating the use of magnetic separation (MAG*SEP) schemes to solve this problem by removing metals present at low concentrations (parts per billion) from groundwater. Argonne is evaluating and further developing a technology owned by Bradtec, Inc., that involves washing the soil with a proprietary solvent (ACT*DE*CON^{SM}) to extract the metals in a liquid, non-hazardous phase. The contaminant is then transferred, by ion exchange, onto magnetically charged, resin-coated particles (MAG*SEP) that are finally removed from the solution by electromagnetic separation **(603-001, 588-001)**.

Removal of volatile organic compounds (VOCs) from contaminated groundwater presents another challenge in environmental cleanup. Argonne has evaluated a membrane-assisted extraction system (MASX) coupled with a membrane-assisted distillation system (MADS) for decontaminating groundwater. Volatile organic compounds in the groundwater are extracted in the MASX unit using sunflower oil. In the MADS, the VOCs are stripped from the sunflower oil, which is then recycled to the MASX unit. Argonne measured thermodynamic properties for the sunflower oil VOC system and completed an energy balance and a material balance for a prototype unit **(446-001)**.

Phytoremediation is an emerging cleanup technology that is based on the well-known ability of plants to take up and concentrate contaminants in their tissues. Hyperaccumulator plants are grown to "biomine" the contaminated soil, and are harvested and treated to further concentrate the contaminants prior to final disposal. Currently, the major drawback of phytoremediation is the slow rate of decontamination. Argonne's innovative approach is in integrating the traditional phytoremediation concept with other technologies to enhance the bioaccumulation by irrigation, fertilization, alteration of the soil's chemical/physical conditions, and/or the use of nontoxic chelating agents. The challenges are to avoid the transport of contaminants deeper into the subsurface, to deliver the chelating agents throughout the soil, and to control the transportation of the chelated metal from lower soil horizons into the root zone **(603-002)**.

Along similar lines, bioreactors, modeled on saline wetland ecosystems, can be used to clean up saline water usually produced with natural gas. Bioreactors employ hydroponic techniques to filter and sequester contaminants and reduce wastewater volume through enhanced evapotranspiration. Our studies indicate that the ideal plant is a vigorous, salt-tolerant species, with a large surface area of transpiring tissue and a dense, fibrous root system that functions as a biological filter **(074-002)**.

Argonne is investigating ion exchange resins for removal of organic wastes from industrial wastewater process streams. Once these wastes are removed, the organic constituents are reclaimed for recycling. Life-cycle analyses are being performed to establish the long-term capacity of the resins for contaminant removal and to evaluate process economics **(176-001)**.

New chelating agents are being designed, synthesized, and characterized for water-soluble heavy metals and the study of actinide coordination complexes as solids and solution species. These complexes are important for separating, recovering, or isolating actinides from other elements. Glove boxes and inert-atmosphere enclosures are used to handle highly radioactive materials. Oxidation-reduction, acid-base, and coordination properties are elucidated by thermochemical, electrochemical, crystallographic, and spectroscopic studies to characterize actinide species (e.g., uranium and plutonium) in environments that model nuclear-waste conditions **(100-002, 099-001)**.

Similarly, new solvent extractants are being synthesized and investigated for their ability to selectively and efficiently extract a wide range of metal ions from acidic media. Argonne researchers are also studying the influence of various diluents on extraction efficiency and selectivity and adapting selected extractant-diluent combinations to extraction chromatographic systems for use in identifying radionuclides (in bioassay and environmental samples) **(206-001)**.

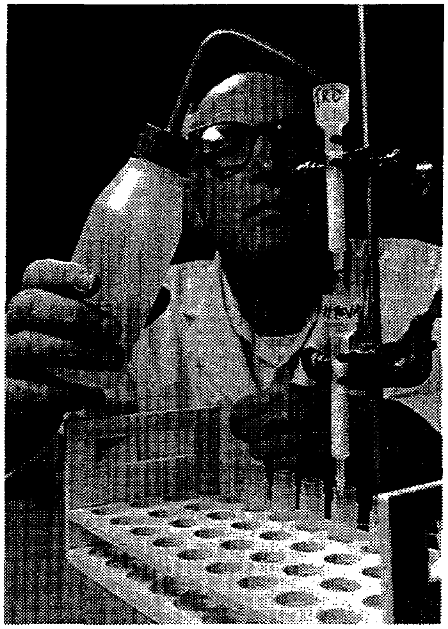

FIGURE 15 Resins concentrate trace contaminants **(206-001)**

After use, complexing/extraction agents should be destroyed in order to recover the metal and avoid contaminating the environment with the complexant. Argonne is investigating the use of powerful oxidants, both commercial and specially designed, to destroy the agents. A major goal is to use the information acquired in this study to design new complexing agents that areboth efficient binders of metal ions and, at the same time, are readily degraded by reaction with strong oxidizing agents **(101-002, 102-001)**.

Argonne is developing processes to recover Mo-99, a common medical isotope precursor, from the fission of low-enriched uranium (LEU). The use of LEU targets in place of high-enriched uranium (HEU) targets is dictated by nuclear proliferation concerns. Two LEU targets are being developed: uranium metal foil and uranium silicide targets. Argonne is establishing chemical methods to recover the Mo-99 from the irradiated targets. The metal foil targets will be treated by an acid dissolution process, followed by precipitation and chromatography separation. The steps in the process are similar to those in Union Carbide's Cintichem process, which is now used for HEU targets containing uranium dioxide **(454-002)**.

Bradtec, Inc., has joined Argonne in developing methods to separate transuranics (TRU), heavy metals, and fission products from waste streams using magnetic microparticles. The ferromagnetic particles are coated with (1) either a selective ion exchange material or an organic complexant containing solvent for the removal of Cs and Sr, or (2) solvents for selective separation of TRU and toxic metals. We are now working on methods to remove contaminants stored in tanks at Hanford and other DOE sites. The greatest benefit of this technology is that the radionuclides and heavy metals can be separated from different types of wastes by using a simple, cost-efficient process without generating large secondary waste streams. The same processes can be adapted and applied to many types of industrial waste streams (e.g., textile, steel, and other metal industries) **(204-001)**.

Researchers at Argonne have been using a new membrane technology called electrodialysis, an electric-field-driven process that uses ion-exchange membranes to remove or concentrate salt from solution. Electrodialysis can produce a much more highly concentrated brine (up to 20%) and may be less susceptible to fouling problems **(557-001)**.

Gas Separations

Argonne is working at recovering chlorine and hydrogen from waste hydrogen chloride streams through electrochemical membranes. The gas stream that contains the hydrogen chloride comes in contact with the cathode of the electrochemical cell. At this electrode, H_2 is produced along with Cl^-. The chloride ions enter the electrolyte, which is composed of metal chloride mixtures held in an inert membrane, and migrate to the anode, where Cl_2 is produced **(201-008)**.

The Laboratory has developed state-of-the-art facilities, techniques, and test procedures to evaluate the structural reliability of hot-gas filters made of monolithic ceramics and ceramic-fiber-reinforced composites. We conduct mechanical testing to assess filter reliability and perform stress and fracture mechanics analyses to establish structural requirements for candidate filter materials. Hot-gas filters are critical elements for the success of combined-cycle power generation with coal gasification **(498-002)**.

Heat Transfer

Argonne's heat transfer research includes both long-term projects to develop new heat-transfer technologies and near-term, more applied, cooperative projects with industry that employ our specialized capabilities to address specific industrial problems. Examples include an effort to develop corrosion control/inhibition strategies in aqueous heat-transfer and energy-conversion systems **(526-001)** and to develop a process to quickly and economically screen vacuum gas oils for corrosive acids. We are also working with Heat Transfer Research, Inc., Shell Development Co., and Chevron Research and Technology Co., to mitigate the fouling of petroleum refinery heat and mass transfer equipment. This effort is based on Argonne's basic Thermal Sciences Program, which has been helping to improve our understanding of the underlying causes for the fouling of organic fluids. The goal of the program is to enable industrial end-users and equipment suppliers to decrease capital and operating expenses and to increase plant availability **(257-001)**. Related projects include an investigation into the use of radio-frequency drying as a means of dewatering municipal sludge **(449-001)** and an effort to develop efficient, compact evaporator/concentrator technology for minimizing waste streams **(450-001)**.

Ongoing heat transfer research **(257-001)** addresses heat exchanger fouling in heavy oil and residual processing. In particular, researchers are studying the effects of sulfur and iron compounds on the kinetics of fouling precursor formation. In a closely related project **(172-001)**, we are investigating fouling in crude preheaters and feed/effluent heat exchangers for hydroprocessing. Argonne also is developing high-performance, compact evaporators and condensers **(258-001)** and incorporating these novel heat-transfer devices into existing unit operations.

We are also conducting basic studies of boiling flows in confined spaces (a few millimeters or less) to generate improved heat transfer correlations for the design of high-efficiency heat exchangers **(276-001)**. These heat exchangers could be used for space conditioning and for specialized miniature cooling devices in microelectronics and materials processing. These studies are supported by an extensive modeling capability in the area of boiling heat transfer for water and liquid metal (static and flowing fluid) for the various heat transfer regimes **(264-001)**.

Some of the longer-range projects include the development of advanced energy transmission fluids for improving the performance of thermal energy transport in piping systems from source to load. This process involves using a phase-change slurry comprising particles of high heat of fusion to greatly increase the deliverable energy density of pumped media compared to pumping hot or chilled water **(263-001)**. The Argonne Slurry Flow Test Facility **(219-001)** has been used to characterize flow behavior, pressure drop, and heat transfer associated with dispersed or highly loaded slurries. The slurries can be heated or cooled, and particles as large as 10 mm can be pumped. We have shown that friction-reducing chemical additives are capable of reducing pipe turbulent flow pressure drop for pure liquid or slurries by as much as 80% when used in concentrations as low as 100 ppm. These concepts allow considerable downsizing of thermal systems piping, energy storage tanks, and pumps and lower energy consumption and operating costs. Through the program, scientists are developing ice slurry heat-transfer technology **(266-001)** to replace chilled water in district cooling applications.

Sensors

Sensors for on-line process monitoring are needed for efficient process control and for development and validation of computer models. Effective sensors are the cornerstone of waste minimization and enhanced recycling (minimization of unwanted by-products) in chemical processing. Argonne has initiated several programs to examine the underlying science and develop new, innovative products in the area of sensor technology.

Stack Gas Monitors

Monitoring the release of gaseous emissions from stacks is required by U.S. Environmental Protection Agency regulations; this monitoring can also affect process efficiency. A number of different types of stack gas monitors have been (or are currently) under development at Argonne.

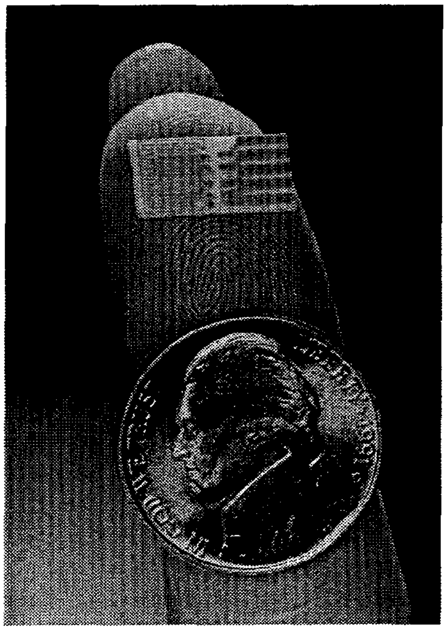

FIGURE 16 Rugged, electrocatalytic gas sensor **(351-003)**

Argonne scientists recently developed a real-time monitoring instrument using FTIR technology to detect gaseous emissions from incinerators and other stacks. This instrument will detect organics and selected inorganics such as HCl, CO, CO_2, and SO_2 at low-ppm or high-ppb levels **(596-001)**. Alternatively, passive-remote FTIR uses ambient energy to detect the molecular absorbance or emission of organic vapors **(598-001)**. The prototype electrocatalytic gas sensors are constructed of advanced, rugged, ceramic metallic (cermet) materials using proven thick-film techniques **(351-002)**. This new sensor technology has shown distinct, reproducible responses to a variety of organic gases and vapors **(472-002)**. We have also developed a novel, low-cost, electrocatalytic gas sensor about the size of a grain of rice that has the durability and lifespan required for field use **(351-003)**. Another type of sensor generates a unique electrical signal representative of a gas or gas mixture "on demand" by using a cyclic voltammetry measurement technique. Neural network signal-processing algorithms match these signals to a gas signature library **(472-001)**. Yet another system relies on millimeter-length electromagnetic waves that produce a molecular "fingerprint" for each chemical compound. This method is capable of detection sensitivity at the parts-per-million level **(014-003)**. One final sensor system for in-place monitoring of stack gas emissions is based on a highly miniaturized time-of-flight mass spectrometer system **(167-001)**.

A unique analytical method for reliable measurement of alkali vapors in pressurized fluidized-bed combustion flue gas has been developed by Argonne researchers **(459-001)**. The analytical activated bauxite sorber bed (AASB) technique requires no sampling line, which eliminates potential alkali-vapor condensation in the sampling line and/or reactions between the alkalis in the sample gas and the stainless steel sampling line. The AASB technique can also effectively differentiate particulate alkalis (present in the fly ash) from vapor-phase alkalis. The technique has been successfully demonstrated in tests conducted in ANL's laboratory-scale PFBC facility and the 15-MW(t) Component Test Facility at ABB Carbon AB, Sweden. Prototype instruments are under development for several applications.

Special Purpose Sensors

Argonne has come up with several unique sensor systems for specific applications. An innovative electrochemical process overcomes the limitations of conventional electrorefining and electrowinning and could lead to an improved capacity to purify a variety of metals and molten salts. The key component is an ion replacement electrode that allows separation of metallic element electrotransport into two steps: an anodic dissolution step and a cathodic deposition step **(435-001)**. In similar research, high-temperature sensors have been designed to withstand immersion in 500°C molten salt and cadmium **(446-002)**. Another sensor, the ultrasonic viscometer, is a patented instrument for in-line nonintrusive monitoring of fluid density and viscosity **(232-001)**.

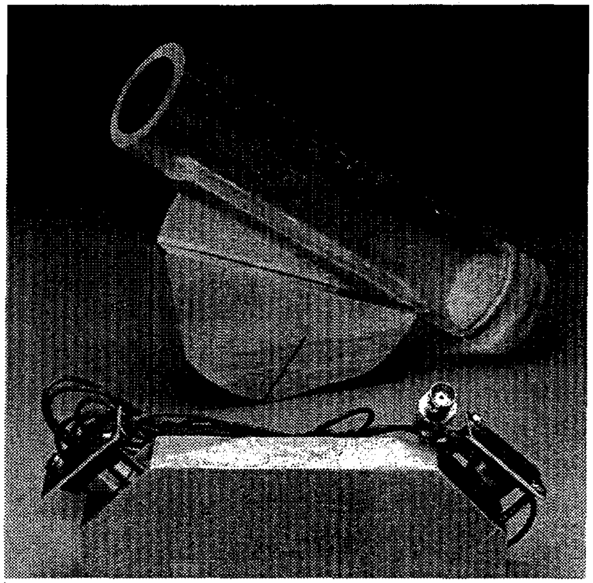

FIGURE 17 Nonintrusive ultrasonic viscometer (232-001)

The combination of MRI and computational modeling methods can be used to characterize the dynamic flow properties and transport phenomena in complex environmental or process systems. Argonne's study focuses on three-dimensional MRI to measure in-situ saturation characteristics, flooding and breakthrough curves, local degradation rates, and transport characteristics of pollutants in porous media **(163-0011)**. Fourier transform Raman spectroscopy is especially suited for on-line analysis of new and recycled plastics **(124-001)**.

ANL has recently developed a relatively small and inexpensive nondestructive probe, based on an associated-particle, sealed-tube neutron generator and gamma-ray energy and flight-time spectroscopy, that can be used to identify and create images of many different elements. The probe can be used to detect drugs, explosives, nuclear and chemical weapons and materials, pollutants, and radioactive waste **(001-005)**. Argonne has also developed a portable radioactive neutron source that can be switched off and on and cycled like an accelerator. The unit could replace standard radioactive neutron sources or accelerators in nondestructive analysis equipment based on neutron activation; it could also provide increased functionality, reliability, and portability **(066-002)**.

Generic Sensor Development

Besides the examples described above, Argonne is involved in a number of projects to investigate more generic sensor opportunities **(072-001)**. The Laboratory has industrial monitoring and process control capabilities to perform analyses, develop products/processes, conduct experimentation, design and construct prototypes, conduct functional testing, and perform diagnostics for the development and improvement of industrial processes **(708-001)**. Sensor development efforts focus on real-time, non-intrusive, and remote-sensing techniques that include acoustic/ultrasonic, electromagnetic, optical, and piezoelectric/pyroelectric technologies. Completed sensors include: (1) ultrasonic and capacitive flow meters, (2) level and temperature sensors, (3) micro-mass spectrometers, (4) ultrasonic viscometers, (5) microwave radiometers, (6) millimeter-wave chemical sensing systems, (7) surface acoustic wave chemical sensors **(120-002)**, and (8) smart-material sensors **(466-001)**.

Analytical Chemistry

Analysis and analytical chemistry are critically important in chemical process monitoring and control. They differ from sensor development in that detailed characterization of chemical processes and products rather than on-line, real-time monitoring, is the objective. There are six specific categories of Argonne's analytical chemistry program, including generic analysis.

Mass Spectrometry

Laser desorption mass spectrometry is used to probe the molecular and elemental distributions of surface and near-surface polymer regions. The Fourier transform mass spectrometer includes microscopic imaging and is capable of micron-level spatial resolution and a mass resolution of greater than 1,000,000 **(407-002, 559-002)**. Secondary neutral mass spectrometry is also used to probe the molecular and elemental distributions of surface and near-surface regions. Analyses can be performed with single monolayer depth resolution and submicron lateral resolution. The instrument is capable of detecting concentrations below the parts-per-billion level **(398-001)**.

Argonne has acquired extensive experience in gas chromatography mass spectroscopy by characterizing complex mixtures such as fossil fuels and synthetic and natural polymers. High-molecular-weight materials, such as polymers, are analyzed by on-line pyrolysis. In addition to performing routine work on a quadrupole spectrometer, Argonne scientists can employ a very high-resolution sector mass spectrometer to dramatically enhance the data obtained by providing empirical formulas for all the mass peaks. Elemental and molecular weight data for large molecules can be obtained by using a number of soft-ionization techniques including the following: desorption chemical ionization, fast atom bombardment, and low-voltage electron impact. Argonne has also developed computer algorithms to analyze these complex data sets. The ability to operate at high GC temperatures also extends the accessible molecular weight range **(167-002, 168-001)**. We are using inductively coupled plasma/mass spectrometry combined with extraction chromatography (also developed at Argonne) to detect long-lived radioisotopes (half-life greater than about 1,000 years) in soil and water **(000-002)**.

Magnetic Resonance

The NMR facility at Argonne is equipped with six NMR spectrometers. A Nicolet 200-MHz (4.7-Tesla) system is used for routine proton NMR analyses; this system is equipped with multinuclear liquid and solid probes. A Brüker 300-MHz (7.05-Tesla) system, also available for general use, has proton and multinuclear capabilities for both liquid and solid samples. A GE 300-MHz (7.05-Tesla) system is equipped with a switchable multinuclear probe for use in multidimensional experiments. Argonne's new 500-MHz system, manufactured by Brüker, has several advanced capabilities, including two- and three-dimensional spectroscopy, multinuclear analysis, spin diffusion measurements, imaging, and gradient-enhanced spectroscopy. A Brüker

100-MHz (2.3-Tesla) system has been equipped with a versatile pulse programmer, 1-kilowatt gradient amplifiers, and an imaging probe containing XYZ gradient coils capable of producing linear field gradients of 58 Gauss/cm to provide microimaging of solid samples **(164-001)**.

Argonne has also developed MRI techniques for both liquid and solid materials; these techniques have been applied to the study of polymer blends and composites, ceramic processing, catalyst fouling, and fuels research. MRI techniques have also been implemented to provide a new window into the transport of solvents in rubbery and glassy polymers and are helping us understand many important industrial processes, such as upgrading heavy hydrocarbons, film casting and coating technologies, development of photoresistors, design of drug delivery systems, and development of solvent-resistant polymers **(165-001)**.

The optically detected nuclear magnetic resonance technique combines the advantages of site-selective optical spectroscopy with the resolution of conventional NMR and the high sensitivity of laser-induced fluorescence and resonant Raman heterodyne techniques **(151-002)**. Argonne has also applied Fourier transform electron paramagnetic resonance (EPR) spectroscopy; pulsed EPR spectroscopy; and NMR of solid, liquid crystal, and liquid phases to the study of organic conductors and conducting polymers **(103-001)**.

Spectrophotometry (including Laser Applications)

The ability to direct energy sources, such as electrons, photons, and energetic ions, to modify and probe surface composition and topography is at the center of many important industrial processes. In this program, researchers use the directed energy to study the properties of materials and develop new procedures for analyzing materials. Particular prominence has been achieved in the application of laser beam technologies to analyze surface impurities; these procedures allow detection at the part-per-trillion level in many cases **(010-002)**.

Laser techniques using variations in wavelength, pulse length, and power density have the potential to overcome the limits of traditional mass spectrometry ionization techniques. The key to successful mass analysis of large nonvolatile molecules is to produce gas-phase ions. The most important advantage is the selection of classes of compounds that can be facilitated using two-photon laser desorption mass spectrometry **(169-001)**.

Diffraction/Synchrotron Radiation

X-ray absorption spectroscopy provides a powerful probe of both the electronic structure and coordination of the absorbing atom. Using this process, scientists can examine the chemical state of catalysts under reactive conditions; the technique is being used to investigate reactions at the atomic level **(179-001)**. Argonne researchers are also using synchrotron radiation X-ray absorption fine structure (EXAFS) to determine element-specific oxidation states and coordination environments. The pivotal aspect of this technology is that, by using combined electron-yield/fluorescence/transmission techniques, scientists can simultaneously study near-surface regions, bulk structures, and electronic properties of catalysts, engineered materials, ore, reservoir minerals, and other materials **(141-001)**. Focused or collimated X-ray beams from synchrotron sources are used to determine the composition (via fluorescence) and crystal structure (via diffraction) of structures on a micron scale. This allows the detailed study of interfacial regions in diffusion zones and positive identification of intermetallic structures and other structures **(536-001)**.

Mössbauer-effect spectroscopy provides a unique analytical capability for nondestructive, element-specific characterization of the electronic, geometric, and magnetic properties of bulk solids and solid surfaces. We have significant first-hand experience in solving commercial/industrial problems related to the corrosion products of iron and its alloys and in identifying iron-bearing phases in oil reservoir formations and production solids. These capabilities are also available for tin-, europium-, antimony-, and neptunium-bearing solids, including amorphous and crystalline powders, foils, films, fibers, frozen solutions, etc. **(141-003)**.

Small-angle neutron scattering analysis is used to examine the size and shape of molecules in solution over a range of temperatures and pressures. The radius for spherical shapes, the cross-sectional radius for elongated shapes, and the thickness for lamellar shapes can be determined by using Guinier analysis. The technique is applicable to a wide variety of solids and complex mixtures in solution **(171-001)**. Scientists in the neutron and X-ray scattering group investigate the static and dynamic structure of crystalline and amorphous solids, liquids, polymers, surfaces, and thin films and the relationship of this structure to other physical properties. Neutron scattering investigations are performed principally at the Intense Pulsed Neutron Source (IPNS). However, other pulsed neutron sources, research reactors, and synchrotron light sources at other laboratories are also used for experiments in which those facilities offer advantages over IPNS **(010-008)**.

Microscopy

The Electron Microscopy Center for Materials Research, an integrated research center at Argonne, has three major objectives:

- Providing scientific and technical support, together with state-of-the-art instrumentation to further materials research;

- Through the High Voltage Electron Microscope–Tandem Accelerator User Facility, providing access to unique research instrumentation for the simultaneous use of ion beam irradiation and electron microscopy; and

- Facilitating dynamic in situ studies of microstructural changes resulting from electron and ion irradiation, mechanical deformation, and gas/solid reactions in materials through direct observation using high-voltage electron microscopy **(010-003)**.

A new area of research is currently underway that, for the first time, employs scanning transmission X-ray microscopy methods to spatially map the chemistry of carbon, oxygen, and nitrogen functionalities in composite materials to a resolution approaching 60 nm. Argonne is also working on systems containing calcium and molybdenum (among other metals). In addition, localized absorption microspectroscopy, recorded at element-specific absorption edges, has allowed scientists to analyze the variations in fundamental chemistry at material interfaces and within composite boundaries. Future studies will focus on the study of reacting systems and applications to dispersed catalyst systems **(181-001)**. One recently developed optical imaging technique, near-field scanning optical microscopy, overcomes the conventional far-field diffraction limit of resolution of 200 nm and allows subwavelength resolution of 12 nm, while preserving all of the traditional advantages of optical microscopy. The numerous potential applications of this technique include fluorescence imaging of living cells and DNA, structural and dynamic studies of cell membranes, super-resolution lithography, and spectroscopy of nanoscale materials **(380-001)**.

General Analysis

Argonne's Analytical Chemistry Laboratory (ACL) provides a broad range of analytical chemistry services to support the scientific and engineering programs at the Laboratory. The ACL also conducts research in analytical chemistry; develops analytical instruments and methods; and provides analytical services for governmental, educational, and industrial organizations. The ACL offers solutions to chemical analysis problems in materials characterization, process definition and control, environmental monitoring, and waste analysis **(182-002)**.

One method frequently used at the ACL, gas chromatography/matrix-isolation/infrared spectroscopy (GC/MI-IR), combines the ability of capillary GC to separate the components of complex mixtures with the high sensitivity and specificity of MI-IR. In this technique, developed at Argonne, a GC column effluent containing 1% argon travels through a glass-lined transfer line and is sprayed directly on a cryogenic collector. The collector, a mirror-finished, gold-plated carousel, is slowly rotated by a computer-controlled stepping motor. This action produces a strip of frozen argon in which the sample molecules, which are surrounded by the argon matrix, retain their capillary column separation. Once the sample is trapped in the matrix, the infrared spectra of the compounds — numbering a hundred or more — can be measured. The MI-IR spectra are free of band-broadening or perturbations caused by rotation or intermolecular forces, such as hydrogen bonding. The GC/MI-IR has nearly the same sensitivity as GC/MS, and the data complement mass spectral data. The GC/MI-IR is ideal for distinguishing between organic isomeric compounds **(169-002)**.

The Laboratory is using flow injection analysis (FIA) to develop novel methods for analyzing trace levels of radioactive waste and addressing other environmental characterization and monitoring problems. In trace analysis, FIA has two primary functions: enhancing the analytical range and removing matrix interferences. We are using FIA pre-concentration and separation approaches as a "front-end" for automated sample pre-treatment prior to mass spectrometric and radiometric detection. Benefits from our work include significant sample enrichment, high selectivity, low risk of contamination and exposure in a closed system, simple operation, and a small instrument footprint **(182-004, 440-001)**.

Our expertise also includes analyzing volatile and semivolatile organic compounds, polychlorinated biphenyls, and pesticides at trace levels in environmental and mixed waste samples, soil/sludge, and aqueous matrices. Purge-and-trap/gas chromatography/mass spectrometry is used to measure concentrations of volatiles. Gas chromatography/mass spectrometry and high-performance liquid chromatography/mass spectrometry are used to detect semivolatiles. Gas chromatography/electron capture detection is used to analyze polychlorinated biphenyls and pesticides **(182-001)**.

We have developed several nondestructive evaluation techniques that can identify material property changes during manufacture and detect critical flaws in manufactured materials to improve processes, ensure quality, and predict the lifespan of certain materials. The chief techniques are ultrasonic imaging, X-ray microcomputerized tomography, magnetic resonance imaging, neutron diffraction, photothermal imaging, millimeter-wave imaging, and laser scatter imaging **(012-003)**.

Argonne has successfully used analytical and scanning electron microscopy, X-ray diffraction, and secondary ion mass spectrometry to identify phases containing radioactivity, perform quantitative analyses, detect trace elements, and obtain chemical state data for many elements **(142-001)**. These analyses can be performed for individual particles as small as 0.1 micron. Argonne has used these methods to assist in several soil remediation projects by showing why certain soil-washing methods were not effective and by suggesting more effective procedures **(613-001)**. We also have high-precision calorimeters for measuring enthalpies of reaction and solution **(079-001)**.

Data Management

ANL has developed information and database management tools for a wide variety of applications — including military logistics, inventory control, treaty compliance, cost-benefit analyses, and decision support for such diverse activities as electric utility dispatch, future investment strategies, or trend and root-cause analyses. Much of this technology can be applied to large corporate and scientific information databases. ANL has also developed software tools that provide a flexible environment for graphically-oriented applications **(226-001)**. This object-oriented language allows the user to create interfaces for text retrieval, geographic information management, decision analysis, planning, lessons-learned analysis, and systems modeling; it also encourages the development of reusable and maintainable code.

Some examples of the information and database management tools include a transportation model **(228-001)** to determine the ability of a region's infrastructure (road, rail, nets) and asset (sea and air) lift allocations to support a proposed activity. This tool is currently being expanded to allow for more detailed inventory tracking. Another example is a treaty compliance and monitoring system **(230-001)** that enables U.S. organizations to create treaty notifications and provides communication and approval processes. This system also creates a central database of treaty notifications and other treaty-related data. Cost-benefit analysis is addressed in a third program **(358-001)** to evaluate alternatives in terms of projected short- and long-term costs. In a related program, a power systems model **(676-001)** has been developed to evaluate the impacts of marketing alternatives, including utility dispatch, spot market transactions, hydrodam operations, and capacity expansion. ANL has developed decision support systems for future investment strategies and capabilities, for the management/distribution of existing funds, and for evaluation of historical information to identify trends and existing resources **(372-001)**. Finally, we created a PC-based system using a custom-designed, U.S.-map-based graphical user interface coupled with a robust commercial information retrieval engine **(372-002)** to rapidly search oversight documentation, to assist in root-cause analyses, identify trends, and efficiently respond to Freedom of Information Act queries.

Finally, Argonne has extensive expertise in developing and implementing client/server databases to manage equipment and facility maintenance. These applications are useful for any manufacturing, power plant, or research and development environment where properly maintained equipment plays a key role in the facility's success **(721-001)**. We have created modules for planning and scheduling preventive, predictive, and corrective action activities and for performing on-line (paperless) procedures; these include preparation, review and signature, and on-line use of the procedure while performing varied maintenance activities. Data collected from preventive and predictive activities can be automatically logged and analyzed and are compatible with wireless input and display terminals **(362-001, 366-002)**.