## Some Examples of Accomplishments Under the

## Basic Energy Sciences Program During 1982

While these selections may not reflect the full range of the basic research carried out through more than 1200 projects supported by Basic Energy Sciences, they are examples of how basic research can be brought to bear to resolve a variety of energy problems.

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## 1. Coexistence of Ferromagnetism and Superconductivity Observed for the First Time Using Neutron Scattering Techniques

Using neutron scattering techniques, a new phase of matter in which magnetism and superconductivity coexist has been directly observed. This work will provide a better understanding of the interaction of these two ordinarily competing forms of order in materials and may lead to better superconducting magnets and other devices through improved materials. The observation was made in a erbium-rhodium-boron compound, $ErRh_4B_4$, in the temperature range of 0.7 to 1.1°K. It has long been known to materials scientists that spontaneous ferromagnetism creates a magnetic field within the source material while superconductivity expels the magnetic field from the material. Indeed, present theories indicate that the coexistence of these two forms of long-range order in matter cannot coexist. This new investigation, carried out at Oak Ridge National Laboratory on material prepared at Argonne National Laboratory, has directly shown for the first time that ferromagnetism, along with an oscillating magnetic order, and superconductivity coexist in a narrow temperature interval at very low temperatures.

The discovery in 1977 of magnetism and superconductivity in a special class of materials containing three elements has generated considerable interest in the nature of transitions from superconductivity to magnetism, and possible coexistence of these two properties. Neutron scattering has been used at Brookhaven National Laboratory to study the magnetic transitions in a series of $(Er_xHo_{1-x})Rh_4B_4$ alloys (holmium replacing erbium atom for atom). $HoRh_4B_4$, the erbium free compound, was found to be magnetic but not superconducting. From neutron and other measurements, Er-rich alloys were shown to be "reentrant" superconductors, that is, successively displaying paramagnetism, a property of normal metals, superconductivity and normal conducting ferromagnetism as the temperature is lowered.

$ErRh_4B_4$ shows long-range ferromagnetism at low temperatures; however, recent neutron scattering measurements on a single crystal showed the surprising result that ferromagnetism and superconductivity coexist along with an oscillating magnetic order in the small temperature range, 0.7 to 1.1°K. These studies, carried out using the unique capabilities for neutron scattering research at DOE laboratories, are proving to be of fundamental importance in understanding the interaction of magnetism and superconductivity, and have stimulated much new experimental and theoretical interest in this field.

(Argonne National Laboratory, S. K. Sinha, G. W. Crabtree and D. G. Hinks; Brookhaven National Laboratory, C. F. Majkrzak, D. E. Mounton, G. Shirane and W. Tomlinson; Oak Ridge National Laboratory, H. A. Mook; University of Maryland, J. Lynn)

## 2. Method for Inhibition of Intergranular Stress Corrosion Cracking Provided by Mechanistic Study

Fundamental research into causes of intergranular stress corrosion cracking (IGSCC) of structural metal alloys in aqueous solutions contaminated with sulfur species showed how borate ions inhibit the build-up of thiosulfate in a crack in the alloy and that the ratio of borate to thiosulfate ion must exceed a threshold value to inhibit cracking. This mechanistic study is providing guidance for the current evaluation of thiosulfate-ion-induced IGSCC of the nickel-base alloy used in the steam generator at the Three-Mile Island reactor TMI-1, under Nuclear Regulatory Commission support.

Iron-chromium-nickel alloys are structural engineering materials which are used throughout energy plants and are susceptible to structural changes during exposure to high temperatures. In Inconel 600, a nickel-base alloy which is the principal commercial alloy used in steam generator heat exchanger tubing in nuclear reactors, a structural change caused by improper heat treatment is the lowering of the chromium levels at the grain boundaries. When the alloy is then exposed to oxygenated water, a phenomenon known as intergranular stress corrosion cracking (IGSCC) results. In spite of the substantial efforts to understand and avoid stress corrosion of this alloy, failures continue to occur under a wide range of environmental, metallurgical and mechanical conditions.

Brookhaven National Laboratory is conducting fundamental research on IGSCC of engineering alloys in sulfur-bearing aqueous solutions. Earlier work demonstrated that the most important factor affecting IGSCC, other than oxygen level, was the ratio of the concentration of borate to thiosulfate ions in the aqueous solution. The physical basis for this appears to be that the undesirable migration of the thiosulfate into the crack is determined by this ratio through electrochemical characteristics of the ions present. At high borate/thiosulfate ratios, the protective oxide film formed on the alloy in aqueous solutions was found to be stable so the corrosion and alloy cracking tendency would be low. At low ratios, the opposite occurred due to the deleterious effect of thiosulfate on the film stability.

This fundamental research on solution electrochemistry has provided the reactor engineering community with the basic guidelines for its assessment of sulfate-induced IGSCC in the primary heat exchangers of nuclear reactors. Understanding the electrochemistry associated with the borate ion/thiosulfate ion ratio indicated that it could be controlled by the addition of other salts to the reactor cooling water. The Nuclear Regulatory Commission is now supporting work at Brookhaven in this direction, including assessing one specific additive, a lithium-containing salt, for use in qualifying the return-to-service of the thiosulfate-contaminated steam generator at Three Mile Island TMI-1 reactor.

(Brookhaven National Laboratory, H. Isaacs, R. Newman, and K. Sieradzki)

3. Improvement in Sulfur Isotope Ratio Measurements Significant for Identifying Acid Rain Sources

Coal is plentiful but coal combustion pollutes the atmosphere. Sulfur contaminants form sulfur oxides upon burning which contribute in part to "acid rain." Sulfur emissions contain varying sulfur-32/sulfur-34 isotope ratios depending upon the source. The ratios are different for sulfur derived from microbial activity, geologic emissions, or fossil fuel combustion. Thus, the isotope ratio gives an indication of the source of the pollutant. It has been difficult, however, because of the excessively long measurement times required, to use sulfur isotope ratio determinations for source identification. In a basic research program in analytical chemistry at the Idaho National Engineering Laboratory, scientists have discovered a technique to make faster and far more precise sulfur isotope measurements.

A thousand-fold improvement has been achieved in measuring the sulfur-32/sulfur-34 isotope ratio. Previous measurements had been made by positive ion mass spectrometry. In the new technique, sulfur oxides are caused to react with fluorine to form sulfur hexafluoride. Because this is a heavier compound which easily picks up electrons, it can be readily analyzed in a negative ion mass spectrometer. With the improved sensitivity, much shorter measurement times are required and thus determination of sulfur-32/sulfur-34 isotope ratios in air is feasible.

(Idaho National Engineering Laboratory, J. E. Delmore)

4. Experimental Observation of "Hot Carriers" Could Lead to Doubling Efficiency of Photoelectrochemical Solar Devices

Photoelectrochemical systems convert solar energy to electrical or chemical energy. Scientists have developed a number of promising photoelectrochemical systems but they are far too costly for the amount of energy output. Research is being carried out at the Solar Energy Research Institute (SERI) to understand fundamental properties of photoelectrochemical systems.

A phenomenon known as "hot carrier effects" has been observed experimentally for the first time in photoelectrochemical systems. Hot carriers had been known in semiconductor solids but it was doubted that they could exist at a solid/liquid interface. Hot carriers are electrons in semiconductors which have been formed with more energy than necessary to excite the charge across the band gap. (The band gap is the difference between certain energy levels characteristic of each semiconductor.) Ordinarily, such electrons become "thermalized", that is lose energy and assume the temperature of their surroundings, before being ejected into solution. As "hot carriers" they retain some of the excess energy as they go into solution. Thus, the theoretical maximum efficiency for solar photoelectrochemical energy conversion using hot carriers is 66%, while the maximum efficiency with thermalized carriers is 31%. In addition, hot carriers can initiate chemical reactions that thermal electrons cannot.

The knowledge that hot carriers can exist at semiconductor/liquid interfaces will be useful to SERI and other scientists who are working in this area for designing more efficient photoelectrochemical systems.

(Solar Energy Research Institute, A. J. Nozik)

5. General Purpose Computer Program to Assist Human Reasoning Processes Used to Evaluate Nuclear Power Plant Systems Designs

Mathematical models of energy systems are used extensively throughout the DOE to gain insight into complex physical processes that are too dangerous, too expensive, or impossible to study experimentally. Usually, these models are solved numerically on large scale scientific computers.

Recently, researchers (computer scientists and mathematicians) at Argonne National Laboratory (ANL) have demonstrated that an Automated Reasoning Assistance Program (AURA) capable of manipulating symbolic logic equations can substantially reduce the human effort required in the analysis of complex systems, such as nuclear reactor safeguard systems and electronic circuits.

The AURA program operates on a set of general rules for manipulating logic expressions describing a complex system. Once a system is described in a suitable notation (e.g., a network of pipes and valves in a reactor cooling system), AURA is able to assist an analyst in proving that sequences of potentially dangerous events will not result in a failure of the backup system.

This theorem proving program is not specialized for one particular application. It has been used in electronic circuit design, verification of computer programs, and to solve several open questions in advanced mathematics. The ANL program is widely acknowledged to be the most flexible and powerful reasoning program yet devised.

Automated reasoning programs such as AURA have a tremendous potential in assisting humans to manage extremely complex systems of every sort, from power distribution networks to reactor systems to computer programs. Because the program provides mathematically rigorous proofs instead of numerical approximations, the results will be much more reliable and precise.

(Argonne National Laboratory, L. Wos and S. Winker)

6. Scientific Feasibility Demonstrated for Producing Batteries With Electrodes Made of Polyacetylene Sheet

The use of storage batteries in many applications has been constrained by practical limitations on size, cost and, especially, weight. An obvious example, of course, is the electric automobile. The idea that lightweight batteries might be developed from certain types of plastic materials grew out of basic scientific studies at the University of Pennsylvania on the electrochemical and physical properties of polyacetylene, an organic polymer material which can be plastically molded into any desired shape. The initial research at this basic level was supported by the Office of Naval Research, the National Science Foundation, and the Defense Advanced Research Projects Agency. The proof-of-concept research for the battery application is being supported by the Division of Advanced Energy Projects in the Department of Energy.

Chemically pure polyacetylene consists of long polymeric chains containing only carbon and hydrogen as chemical constituents. In this form, it is a good electrical insulator; however, the electrical properties of polyacetylene can be radically modified by using electrochemical techniques to introduce controlled quantities of certain other chemical species, as electrically charged ions, into the material. Depending on the concentration of these selected impurities, or "dopants", the electrical conductivity can be varied over a very wide range: from that of an insulator, through the semiconductor range, and finally to values characteristic of metals. Moreover, this process is entirely reversible. In addition to being of considerable scientific interest, these remarkable properties suggested that polyacetylene could well have promise for a new type of storage battery. This was confirmed in subsequent experiments carried out by Professors MacDiarmid and Heeger at the University of Pennsylvania. The experiments indicate that plastic polyacetylene batteries have the potential of delivering ten times the power, with one tenth the weight and one third the volume, as compared with lead-acid batteries. These results led to licensing of the invention to Allied Corporation who announced plans for an intensive program of technology development.

(University of Pennsylvania, A. G. MacDiarmid and A. J. Heeger)

## 7. Progress Attained in Determining How Plants "Sense" Temperature

Green plant photosynthesis represents the principal mechanism by which solar energy is trapped in a form available to man. While plants are adapted to grow in many diverse niches, their growth, and concomitantly their photosynthetic capacity for solar energy conversion, is often limited by adaptation to environmental factors such as water availability, temperature extremes, salinity and numerous others. Thus if the photosynthetic base is to be expanded it is necessary to know how plants adapt to sub-optimal environmental factors.

It has been known for many years that plants may adapt, within limitations, to temperature extremes. However, one of the unanswered questions is how the plant senses temperature. We still do not know the answer to the difficult question, however, some recent insight has been achieved in investigations at Michigan State University by studying mutants of fungal slime molds which are impaired in their ability to sense temperature. The responses observed were ones where the organisms would either migrate towards or away from defined temperature regimes. The results of these studies indicate that these organisms have two sets of sensors for temperature, one at a high range, the other at the low range. The availability of these mutants also affords an opportunity to seek the molecular basis of the sensing response. Understanding the mechanism involved is important in identifying strategies for manipulating plants to expand the base of photosynthetic energy conversion by virtue of extended plant growth either by modifying ambient temperature conditions or being able to extend the use of arable land in currently less desirable temperature regions. The development of such possibilities is dependent upon the understanding of biological phenomena associated with adaptation to temperature extremes and other limiting factors. The present work is a first, but important step, in this long term effort.

(Michigan State University, K. Poff)

## 8. Low Temperature Neutron Irradiation Facility Provides Data Critical for Fusion Magnet Shielding Design

An important construction project in the Fusion Program, the Experimental Power Reactor, (EPR) is under design and the Oak Ridge National Laboratory Low Temperature Irradiation Facility used for neutron radiation damage research on materials has been used to experimentally test the EPR magnet design. Experiments on copper, a principal component in the magnet were carried out under typical gamma ray and neutron irradiation conditions that are expected to exist in the EPR. The low temperature requirement for the experiments occurs because the magnet is a superconductor constructed with both superconducting materials and copper (normal metal) which is refered to as a stabilizer in this system. The magnet "field-on" resistivity, increases under irradiation and the designers recommended that when the increase reaches 25% of the design resistivity, the magnet should be annealed to bring it back to the initial level. They further recommended that five annealing cycles should be the lifetime maximum for the magnet. The experimental program, uniquely possible at the low temperature irradiation facility, led to the conclusion that the five annealing cycles recommended by the designers as a lifetime maximum would be reached in two years.

All recent assessments of fusion magnet materials agree that the least radiation-resistant materials are the stabilizer and the organic insulators.

The stabilizer (normal metal) of a composite superconductor safely carried the current during a localized momentary normalization of the superconductor. The amount of normal metal needed for safe operation increases with increasing resistivity of the metal. As a result, the design of large magnets for fusion reactors will depend sensitively upon increases in the resistivity of the stabilizer produced by irradiation. To minimize these increases periodic warmup of the magnets to remove annealable portions of the radiation-produced resistivity is planned. In response to designers' needs, resistivity changes were studied in specimens of Cu throughout five cycles of an alternate irradiation (4.0°K) and annealing (14 h @ 307°K) program carried out. The results for a type of Cu now in use were used to construct the response of stabilizer resistivity to neutron dose. The gamma-ray and neutron dose scales were adjusted to match equivalent operating time at a typical magnet location in the Experimental Power Reactor (EPR). The limit of a 25% increase in field on resistivity before annealing is required was based on a consensus by designers. From the results it is concluded that the five annealing cycles recommended by designers as a lifetime maximum would be completed in only two years.

The performance data of the Cu stabilizer suggests that additional shielding for magnet protection or magnet-design changes are needed for the EPR. This information is essential for any large-scale fusion reactor design.

(Oak Ridge National Laboratory, R. R. Coltman and C. Klabunde)

9. Ion Implantation Production of Amorphous Layer on Iron Surfaces Greatly Reduces Friction

Ion implantation research has led to a non-crystalline alloy surface modification of several different iron base alloys, which have in turn exhibited superior resistance to friction and wear. Such behavior is required for the reliability of weapons systems involving coded switches, where extended life would yield a significant cost-saving benefit. It could also lead to a reduction in the necessity for the large concentrations of the strategic material chromium that is presently required for wear resistant applications, as well as an extension of the service lifetime for friction and wear resistant components.

Unlubricated friction and wear of ion implanted iron alloys is being studied in amorphous iron:titanium:carbon alloys formed by titanium and carbon implantation. This ternary amorphous layer which is formed by ion implantation was previously discovered at Sandia. Recent studies show that substantial reduction in friction (typically a factor of 2) are obtained for pure iron and for steel surfaces containing this implant-formed alloy. Also for certain alloys, the wear is strongly reduced (e.g., up to a factor of approximately 20 for light loads in 15% chromium-5% nickel steel). Interest in such surface modification treatments stems in part from important potential weapons applications involving coded switches, where extended life could be of considerable benefit. Failures during routine test operations are currently believed to be related in part to wear debris observed in post-failure inspections. Weapons requirements of reliability and minimum space prevent the use of conventional design improvements (e.g., liquid lubricants, bearings, higher torque motors). The current friction and wear studies are being carried out under analogous wear conditions to explore this important area.

(Sandia National Laboratories-Albuquerque, S. T. Picraux)

10. Detailed Measurement of Charged Particle Production by 14 Mev Neutrons Made Possible by a Specially Designed Spectrometer System

Materials bombarded by fusion neutrons are altered by nuclear transformations that produce hydrogen and helium. To assess the potential performance of specific materials for fusion reactor applications, cross-section data are required by the fusion community and the Office of Fusion Energy.

The required cross-sections are difficult to measure because of the relative weakness of available fast neutron beams, the requirement for thin targets to permit the escape of the charged particles produced, and the large radioactive backgrounds associated with fast neutrons.

In order to make much better measurements of the energy spectra and angular distributions of the charged particles under these conditions, magnetic lens systems have been developed, first at LLNL and more recently at Ohio University, to capture, focus, and transport these charged particles from the reaction target to a remote well-shielded detector.

Measurements at the high particle energy of 14 MeV encountered in fusion reactions have been completed for the materials designated to be of interest to the Fusion program, e.g., Li, Be, B, C, N, O, F, Al, Si, Ti, V, Cr, Fe, Ni, Cu, Nb, Mo, Sn, W, and Pb. The measurements made for low mass number nuclides are also of interest to others, e.g., for neutron theory studies. The detector systems have now been improved to such an extent that it has become possible to measure cross-sections at fast neutron energies other than those in the 14-15 MeV range at the very intense LLNL Rotating Target Neutron Sources where this work was carried out. Measurements have been made at the Ohio University high current tandem Van de Graaff at 8 MeV for $^{58}$Ni and 316-stainless steel.

(Lawrence Livermore National Laboratory, R. C. Haight; Ohio University, R. O. Lane)

11. Columbia River Basalts Found to Have Chemical Properties That Significantly Assist in Immobilization of Long Lived Radioactive Elements

The migration of elements in the earth's crust is of vital importance to understanding the possible migration of radioactive wastes from a repository to the biosphere. The chemical behavior of neptunium is being studied to accumulate information on the long term probability of radionuclide migration into the biosphere via groundwater solution and in contact with basalts. A basalt is a fine grained dark rock low in silicon and aluminum, enriched in magnesium and iron. Columbia River basalts have been found to reduce neptunium from a +6 oxidation state to a +5 or +4 state, i.e., to change its chemical behavior, so that it is highly adsorbed on the surfaces of the basalt and thus substantially immobilized and retarded with respect to entrance into the biosphere. The iron in the basalt is in a chemically reduced state and is the active element in the basalt that reacts with neptunium. The reduction of the high oxidation state of plutonium to an immobile form by similar processes might be expected. This finding provides support for the proposed placement of deep nuclear waste repositories in basalts and suggests that ferrous-based materials might be useful as backfill to add an additional safety factor.

(Argonne National Laboratory, N. Susak, A. Friedman, S. Fried and J. Sullivan)

## 12. Accelerated Radiation Damage Study Shows Bulk Swelling of Proposed Nuclear Waste Storage Medium Larger Than Previously Projected

The bulk swelling of the oxide zirconolite was found to be large and in disagreement with the stability inferred from x-ray measurements. The new data may compromise the use of zirconolite in a synthetic ceramic mixture called SYNROC which has been proposed as a waste host, partly based on the earlier x-ray results. Complementary research has provided the first experimental validation of the plutonium "doping" technique, used in the zirconolite study, as an appropriate accelerated test for stability of a waste form under radiation.

A recognized need of nuclear reactor technology is the development of nuclear waste isolation methods which will be secure for geologic times (on the order of one million years) to allow decay of long-lived radioisotopes.

Ceramic waste forms potentially offer this stability. A ceramic mixture termed SYNROC (from synthetic rock) has been proposed as a waste form since it consists of crystalline materials found in nature, known to be geologically stable and capable of being tailored to be hosts for specific radionuclides. One such component, zirconolite, an oxide of zirconium, titanium, and calcium, will retain radioactive elements such as plutonium within its crystalline structure. To predict its long term behavior, it is necessary to evaluate the structural and dimensional stability of zirconolite under irradiation by the kind of radiation to which it will be subjected, in this case alpha rays.

At Los Alamos National Laboratory, zirconolite has been alloyed (or "doped") with the radioisotope plutonium-238 in order to study structural changes such as cracking or phase transitions which might compromise the stability of the waste form. Macroscopic damage has been observed in terms of bulk swelling, viz., about 5 percent swelling after an accumulated dose equivalent to that obtained in one hundred-thousand to one million years in an actual waste. In addition, x-ray measurements of lattice dilation were made for comparison with the bulk swelling. Good correlation was found initially. At higher levels of irradiation, corresponding to longer times, deviations between the bulk swelling measurements and x-ray data were found which were resolved by recognizing that the material had become amorphous and that x-rays would no longer monitor swelling correctly. This finding suggests that conclusions on the radiation stability of zirconolite based on x-ray methods alone are questionable. Specifically, the swelling of one component in SYNROC will probably lead to cracking of the entire waste form. In turn, the ingress of ground water through the cracks, which increase the surface area, will lead to leaching of the waste species by the water over that predicted. In complementary research at Pacific Northwest Laboratory, zircon (a zirconium silicate) also has been doped with plutonium and the damage measured in terms of both lattice dilation and bulk swelling. The laboratory results on doped material agreed with published data on naturally damaged zircon at low dose levels. This correlation is a critical first step in demonstrating that plutonium doping offers a valid accelerated approach to study damage accumulation in actual waste forms, with acceleration being by a factor of one-to-ten thousand over the design dose rate.

(Los Alamos National Laboratory, F. W. Clinard; Pacific Northwest Laboratory, W. J. Weber)

## 13. Leaching of Plutonium From Glass Host Materials Into Water Increased by High Radiation Fields

One of the mechanisms responsible over long time periods for the transport of radioactive species from one location to another is leaching. The radioactive species or any species that is soluble, is dissolved or made mobile by local groundwater and transported to some other location where it precipitates or is deposited. The extent to which this mechanism affects radioisotope movement is important in dealing with long term nuclear waste isolation. Previous studies on the effects of high radiation conditions on the rate at which plutonium can be leached out of materials have dealt with only the solid glass system and water not exposed to radiation for any extensive periods. Recent studies were conducted on an expanded system consisting of the glass which contains actinide elements and an aqueous medium in a high radiation field. These studies have shown that the strong oxidizing and reducing reactants formed during the irradiation of the aqueous medium significantly increase the amount and rate of leaching of plutonium from a standard sample of a glass material. This aspect of the effect of radiation on a glass/aqueous system was not fully recognized heretofore. It has also been shown that a significant fraction of the leached plutonium is associated with colloidal silica particles which also result from the irradiation of the glass. This association could increase the mobility of plutonium from a breached respository. The results of this research provide additional insight important in the design of nuclear waste isolation systems.

(Argonne National Laboratory, J. C. Sullivan)

## 14. Clarified Picture of the Chemistry of Plutonium in Environmentally Important Aqueous Media

All bodies of water contain dissolved carbon dioxide which, on solution, forms either the carbonate or bicarbonate ion. These two species are in dynamic equilibrium with bicarbonate dominating in the more acidic solutions and carbonate in the more basic ones. This dynamic equilibrium tends to maintain the acidity level in the system and is called buffering. A comprehensive picture of the chemistry of plutonium species and certain other actinides in environmentally important aqueous carbonate-bicarbonate media has been developed.

Combination of electrochemical and spectroscopic techniques has produced the first comprehensive picture of the reduction-oxidation chemistry of plutonium and certain other actinides in carbonate-bicarbonate media. Many inland lakes and groundwaters are bicarbonate-buffered; and, this study has identified the environmentally important or stable oxidation states of plutonium in such media to be Pu(IV) and Pu(VI) and not Pu(V). Pu(V) has been found to be stable in the more alkaline, carbonate-buffered media found, for example, in limestone deposits. Natural reducing conditions such as iron deposits can lead to possible immobilization of the plutonium (IV), (V), or (VI) by the precipitation of Pu(III) products. Preliminary studies with uranium and neptunium show few chemical similarities with plutonium and indicate considerable complexities in actinide environmental chemistry. This new insight strongly contributes to our understanding of the behavior of actinides in the environment.

(Argonne National Laboratory, Dennis W. Wester)

15. Natural Soil Substances Shown Likely to Retard Migration of Plutonium and Other Actinides

Studies on the chemical binding of actinide elements to naturally occurring humic materials -- organic portions of soils -- indicate that migration of plutonium through soil rich in humic materials would be very slow. Naturally occurring humic materials are polymeric sustances which are known to bind metal ions well and are found in soils and both fresh and marine waters. Data for absorption of americium, thorium, and uranium ions from aqueous solutions show that the complexing, and hence retention of these ions by the complex organic species in humic materials is strong and increases as the solution becomes more basic. Calculations of the competition for Pu(IV) - plutonium's most probable form - between hydrolysis in the aqueous solution at midrange pH values and binding to humic materials show that the binding is significantly competitive and sometimes dominant at normal environmental concentrations. Further studies of the dissociation of thorium (IV) humate show that a significant portion of the bound metal ion is essentially kinetically inert. Thus, to the extent that Th(IV) mimics the chemical behavior of Pu(IV), these results indicate a very slow migration of plutonium through soils rich in humic materials due both to the high binding constants and the very slow dissociation rate of most of the bound metal ions at low acidities. These and related studies suggest that there exists a variety of geomedia, humates as well as minerals, that adsorb and strongly bind actinides and would restrain their migration from a repository.

(Florida State University, Gregory R. Choppin)

16. Chemical Vapor Deposition Used to Produce Zirconium Diboride with Superior Solar Energy Absorption Properties

A chemically vapor deposited zirconium diboride was prepared at Sandia National Laboratories which is an oxidation resistant high temperature selective photothermal absorber. It has a desirable low infrared emittance and a high absorptivity. By virtue of its higher oxidation resistance it can function at higher temperatures that lead to a greater energy conversion efficiency, and for longer maintenance- and replacement-free lifetimes.

Recent studies on chemically vapor deposited (CVD) zirconium diboride at Sandia National Laboratories show low infrared emittance and high absorptivity, which make it attractive as a high temperature selective photothermal absorber. This research includes oxidation studies to 1600°C in air, measurement of emittance and solar absorptance, characterization of antireflection coatings, and long term stability characterization in air to 600°C. Present results are that zirconium diboride undergoes slow oxidation in air above 400°C, that zirconium diboride has better spectral selectivity (emittance/absorptance ratio) than titanium diboride, that silicon nitride provides a good antireflection coating, and that the zirconium diboride/silicon nitride interface is stable in air to 600°C. Typically, a 20 micron coating of zirconium diboride is deposited by CVD on a metallic substrate and overlay an 0.07 micron antireflective film of silicon nitride on top of the zirconium diboride. As-prepared absorptance was found to be 0.87-0.93 and is 0.87 after 500 hours at 600°C. The as-prepared emittance at 100°C is 0.10 and remains the same after 300 hours at 500°C but changes to 0.16 after 500 hours at 600°C. The Solar Energy Research Institute has requested samples for further evaluation.

(Sandia National Laboratories-Albuquerque, E. Randich)

## 17. <u>One-Step Route for Direct Gasification of Carbon to Methane at Relatively Low Temperature</u>

Conversion of carbon-containing resources such as coal, woodchips, or biomass to natural gas is desirable, but the existing technology is difficult and expensive to implement. In a research program on catalysis at Lawrence Berkeley Laboratory (LBL), carbon reactions at surfaces are being studied in order to generate knowledge that might make such conversions go faster, confine them to desired products, make them easier to carry out and, thus, render them more economical. The project is jointly funded with Fossil Energy.

A promising route for direct conversion of carbon to methane has been discovered. In existing coal gasification technology, carbon is exposed to steam at high temperature to form carbon monoxide and hydrogen, which are then taken through a second step with a nickel catalyst to produce methane. Now the LBL chemists have discovered that graphite, a pure form of carbon, can be caused to react with steam at lower temperature in the presence of a potassium hydroxide catalyst to produce carbon dioxide and methane. The LBL method is attractive because it requires only one step instead of two, and it proceeds at considerably lower temperatures. These advantages point to possible savings of energy and plant equipment.

(Lawrence Berkeley Laboratory, G. A. Somorjai and N. H. Heinemann)

18. New, Organometallic Chemistry May Help Coal Conversion and Industrial Chemicals

Chemical studies have led to (1) long sought-for activation of carbon-hydrogen bonds in saturated hydrocarbons, brought about by insertion of a transition metal atom between the carbon-hydrogen pair of atoms and (2) selective oxygen atom transfer to unsaturated hydrocarbons. The former may be important to activating organic groupings in coal for conversion while the latter suggests more energy efficient processes for making important chemical intermediates.

One of the greatest challenges in homogeneous transition metal catalysis involving hydrocarbons has been the activation of carbon-hydrogen bonds in completely saturated hydrocarbons. Recently, the first stable transition metal complex capable of carrying out direct intermolecular insertion of a metal center into carbon-hydrogen bonds of completely saturated hydrocarbons was discovered. An organometallic iridium hydride complex was prepared which upon irradiation with ultraviolet light underwent loss of molecular hydrogen to generate a highly reactive iridium center that inserted rapidly into the C-H bond of various hydrocarbons including saturated ones. The products have been characterized by spectroscopic techniques. Work is continuing on these reactions with attempts to develop catalytic processes for the conversion of hydrocarbons into other, more highly functionalized, organic molecules. This may be important to the activation of organic moieties in coal.

BES chemists have achieved an advance which could possibly lead to three-fold benefits in the chemical industry: large savings of energy and expense, much less wasteful use of petroleum for petrochemicals and the production of desirable chemicals which were previously difficult to obtain. These chemists have recently succeeded in preparing some palladium nitro complexes that are catlaysts for the selective oxidation of various olefins to ketones or epoxides, which are important industrial chemical intermediates. The advantage of selective oxidation is that it overcomes inefficiencies in use of petroleum derived starting materials that stem from non-selective transfer of oxygen atoms from molecular oxygen to organic molecules in the catalytic cycle. A mechanism has been established for the ketone-producing catalytic cycle. It involves coordination of the olefin by palladium, transfer of an oxygen atom from the nitro complex to the olefin, separation of the product ketone and palladium nitrosyl complex and oxidation of the nitrosyl complex back to a nitro group by molecular oxygen.

(Lawrence Berkeley Laboratory, R. G. Bergman; Brookhaven National Laboratory, M. A. Andrews)

19. Experiments Impact Widely Held Theory by Showing Reaction of Oxygen Atoms With Unsaturated Hydrocarbons Does Not Involve Carbon-Carbon Bond Breakage

A turnabout has been forced on our understandings of an important aspect of combustion chemistry. Molecular beam experiments, supported by theoretical calculations, indicate that the reaction of oxygen atoms with unsaturated hydrocarbons leads preferentially to the formation of reactive species in which the oxygen atom has taken the place of another group in the molecule. Contrary to previous belief, carbon-carbon bond breaking does not occur.

Experimental investigation, under single collision conditions, of the reaction of unsaturated hydrocarbons and oxygen atom has indicated that the dominant reaction is the formation of a free radical in which oxygen atom substitutes for another group on a carbon atom in the hydrocarbon molecule. This is contrary to previously held opinions, based on cruder experiments, that the initial step in the reaction is the breaking of a carbon-carbon bond. This research was carried out with crossed molecular beams and experiments have been performed on a number of unsaturated hydrocarbons. Theoretical calculations done in the same laboratory on the ethylene-oxygen atom reaction completely support the new experimental conclusions. These new results alter our ideas concerning the mechanism of hydrocarbon oxidation with important implications for modeling hydrocarbon combustion. The research was performed by Y. T. Lee, a recent Lawrence Award winner and his collaborators.

(Lawrence Berkeley Laboratory, Y. T. Lee and W. A. Lester)

20. Improved Understanding of Hydrogen Embrittlement Phenomenon and Methods to Prevent it Result from Ion Implantation Research

Ion implantation research at Sandia National Laboratory has led to a better understanding of the factors related to the behavior of hydrogen isotopes and helium gas in several different metals. This is important for the first containing wall and limiters in magnetic fusion energy tokamak power reactors. In addition, ion implanted cesium has shown promise for inhibiting hydrogen embrittlement in stainless steels, and offers a potential solution to an old problem in other technologies.

The ion implantation program at Sandia National Laboratory is impacting on DOE magnetic fusion energy (MFE) funded program co-sited at Sandia. Two important MFE problems concerned with tokamak operation are hydrogen and helium recycle, and tritium inventory. Because a significant fraction of the tritium in tokamak power reactors will be ion-implanted from the plasma into the vacuum walls and limiters, it is important to understand the factors governing release of this hydrogen isotope from the first-wall materials. The two most important processes influencing such release are: 1) trapping of the hydrogen by implantation damage or by impurities, such as helium ejected from the burning deuterium-tritium plasma; and 2) blocking by surface permeation barriers such as oxides. Ion-beam techniques have been developed which allow trapping mechanisms and surface permeation barriers to be quantitatively characterized in a single experiment. These methods have been successfully applied to iron, nickel and, very recently, to austenitic stainless steel, which is often used as the tokamak first-wall material. The experiments in stainless steel quantitatively measured the binding of hydrogen to helium traps and also the effectiveness of the surface barrier as measured by the recombination coefficient. These results bear directly on predictions of tritium recycling behavior in tokamaks. The mechanical embrittlement of stainless steels by hydrogen isotopes is also an important consideration in the design of nuclear weapons. This research has discovered that in nickel, which is considered to be a model system for stainless steel, ion-implanted cesium was found to strongly bind hydrogen.

If cesium can be implanted into bulk stainless steels, it could be expected to inhibit hydrogen embrittlement.

(Sandia National Laboratories-Albuquerque, S. Myers)

21. Synchrotron Radiation Used to Obtain for First Time Both Surface Structure and Temperature Distribution for Silicon on Laser Heating

Intense pulses of laser light incident on the surface of a semiconductor are known to profoundly modify its electrical and structural properties. Though this process, pulsed laser annealing, is a significant new direction for producing electronic components and photovoltaic cells, the detailed processes are not understood. The short time scale (about one one-millionth of a second) of pulsed laser annealing of semiconductors has severely limited the use of ordinary structural studies to resolve the present uncertainties concerning the detailed atomic processes. In seeking to illuminate these processes a new powerful technique has been developed to perform very fast (less than one one-millionth of a second) investigations of atomic structure utilizing the ultra-short (less than one one-billionth of a second, a nanosecond) intense x-ray pulses unique to synchrotron radiation sources. This technique, a major technological accomplishment in itself, provides three orders of magnitude improvement in the time resolution of transient structural measurements.

By synchronizing the ultra-short x-ray pulses from the Cornell High Energy Synchrotron Source (CHESS) with the 15 nanosecond pulses from the heating ruby laser, the thermally induced strain after the laser heating pulse has been observed. A thermodynamical analysis of the x-ray data has provided time-resolved lattice temperatures as a function of depth into a silicon crystal. The results indicate surface temperatures of 1150 and 750°C were found 100 and 195 nanoseconds after the laser heating pulse, respectively. Large thermal gradients as a function of depth were observed, and the rapid cooling of the surface was accompanied by heat flow into the crystal, as indicated by rising temperatures deeper into the crystal.

In a second experiment, similar measurements made on silicon implanted with boron have monitored the structure of the near-surface ( 0.3 m) region directly. This is possible because the surface layer is contracted due to the boron and the scattering of the x-rays is thereby displaced from that of the bulk crystal. The thermal shift of this surface scattering indicated temperatures greater than 1100° about 100 nanoseconds after the laser pulse. The disappearance of the scattering at shorter times, 40-60 nanoseconds after laser pulse show the near-surface region to be noncrystalline (melted).

Both of these experiments support the thermal model of pulsed-laser annealing over the model based on electronic processes. This result should allow more precise design of pulsed-laser annealing and accelerate its use in commercial applications.

(Oak Ridge National Laboratory, B. C. Larson, T. S. Noggle and C. W. White)

22. Molecular Clusters Generated Having Hundreds to Thousands of Molecules Bearing a Single Unit of Electric Charge

Nuclear fusion has the theoretical potential to create large amounts of energy with small amounts of raw material. The science, however, is still in its early stages of development, and although much progress is being made along promising routes, it is still worthwhile to explore other avenues. In a basic research program on mass spectrometry at the Brookhaven National Laboratory, a possible new approach to fusion has been conceived. The project is jointly funded by the Division of Chemical Sciences and the Division of Advanced Energy Projects.

Very large clusters of hydrogen molecules have been generated, each of which contains hundreds of thousands of molecules and one unit of electrical charge. These cluster ions are a new type of chemical species. Produced in a specially built mass spectrometer, they survive as long as they are not allowed to collide with other molecules. Because the clusters contain electrical charge, it should be possible to accelerate them in a properly designed ion accelerator. They can then be made to collide with solid targets or perhaps other cluster ions. This might lead to the creation of microplasmas at extremely high temperatures and thus to conditions needed for nuclear fusion.

(Brookhaven National Laboratory, L. Friedman)

23. Major Advance in Atomic Physics Permits Spectroscopic Study of X-rays Produced at Instant of Collision of an Ion and an Atom

A major advance in atomic physics has opened up an entirely new area of study: quasimolecular x-ray spectroscopy. Highly energetic atomic ions are first slowed, then collided with target atoms. At the moment of collision, x-rays are produced that can be associated with neither projectile nor target species but with a short-lived "molecule" of the two. Spectroscopy of these will add to our understanding of processes important in fusion.

A BNL physicist reports that the study of low energy multiply charged ions using the accel/decel technique has opened up an entire new field of spectroscopy of quasimolecular x-rays in collision physics. Chlorine ions, each stripped of sixteen of its seventeen electrons and having an energy of 300 kev/amu, were directed into a gas target where collisions produced x-rays that were not identifiable as belonging to either one of the atoms participating in the collision. Instead, the x-rays emitted were identified with a quasi-molecule that is formed and exists only for the period of the collision.

Previously, chlorine ions containing only one electron were produced at 4.5 Mev/amu, an energy so large that the x-rays emitted during collisions were greatly and asymmetrically broadened toward higher energy. This distortion obscured the process involving the transfer of electrons from one collision partner to the other. The x-ray structure observed at the higher energy made it impossible to assign a specific energy value to each of the x-rays produced and to detect the predicted oscillatory dependence of x-ray spectra on the impact parameter.

The new development permits a clear energy assignment to be made and allows for the oscillatory behavior to be documented. The better resolved spectra are necessary to understand the physics that takes place during the $10^{-18}$ sec collision which is 100 to 1000 faster than the transition lifetimes of x-rays emitted by the individual atom.

This development occurred as part of a research effort supported by Chemical Sciences in response to the needs of magnetic fusion energy technology where the physics associated with low energy highly charged ions are not well understood. The accel/decel proof-of-principle was demonstrated earlier by Jim Bayfield at the University of Pittsburgh, then under contract with the Division of Chemical Sciences. As far as is known, the BNL accelerator is the only unit in the world that can conduct this type of experiment. The only other possible competition may come from two laboratories in Germany (GSI and Heidelberg) but it is expected that they will require 3 to 4 years of development before they can obtain similar results. One of these laboratories, the one at Heidelberg, supported members of their staff to collaborate in the BNL experiments.

(Brookhaven National Laboratory, K. Jones)

## 24. Mathematical Theory Shows Onset of Chaotic Phenomena Follows a Precise Law Independent of Size, Boundaries, or Other System Details

Most physical systems are described mathematically by nonlinear systems of equations, including plasma dynamics, electronic circuits, and fluid flow. However, there is no satisfactory mathematical basis for describing turbulence or chaotic behavior -- usually the equations are linearized and approximations are calculated. Recently scientists at the Los Alamos National Laboratory discovered a set of universal constants that apply to a broad class of nonlinear phenomena.

In the last century, the mathematician Poincare' showed that certain complex systems of differential equations are equivalent to low dimensional mappings. In studying the analytical properties of these mappings, the Los Alamos scientists were able to establish that the systems described by these equations can reach turbulent or chaotic states by evolving through a distinct, identifiable series of period doublings according to a set of universal constants. These phenomena occur regardless of the details of the specific systems. Thus in many cases what had been thought of as random behavior exhibited by these physical systems is in fact a well-determined and universal pattern. Experimental confirmation of this universal behavior has been reported in Josephson junction devices, fluid flow experiments, and chemical reactors.

Understanding the mathematical basis of turbulence and chaotic behavior is important in the study of fusion processes, combustion, fluid flow through pipes and porous media, and many other areas of interest in the development of energy systems.

(Los Alamos National Laboratory, M. Feigenbaum)

25. <u>First Detection of Fluorescence Emission From Electronically Excited Plutonium Hexafluoride Has Been Achieved</u>

The first detection of fluorescence emission from electronically excited $PuF_6$ has been achieved. This directly impacts the development of methods for the laser-based separation of plutonium isotopes.

Fluorescence has been observed in an initial study of plutonium hexafluoride vapor using visible wavelength laser excitation. This is the first observation of fluorescence from electronically excited plutonium hexafluoride. The large differences in electronic energy levels and in molecular dissociation limits make it likely that plutonium hexafluoride will not mimic uranium hexafluoride. This has been confirmed in this scouting study of selective laser excited plutonium hexafluoride.

The small fluorescence quantum yield but long fluorescence lifetime suggest that a complex mixture of energy transfer and dissociation reactions simultaneously occur when plutonium hexafluoride absorbs visible wavelength light. Experimental tests of this interpretation are being undertaken and efforts are being made to identify the emitting state. This work directly impacts on efforts to separate plutonium isotopes by providing the first information concerning the dynamics of electronically excited plutonium hexafluoride.

(Argonne National Laboratory, J. V. Beitz)

26. New Process to Recover Silver From Waste Developed Which Meets Stringent Environmental Standards

A new process for silver recovery has been developed utilizing a hypochlorite-hydrazine system that produces greater than 99.99% silver removal from spent fixer. The process not only is important for silver recovery but also meets stringent environmental standards for pollution levels of silver and cyanide in streams.

Nearly 50,000 liters of silver-bearing and cyanide-bearing waste liquids are generated annually at Oak Ridge National Laboratory from photographic and photoreproduction processes. Because the acceptable level for discharge of either silver or cyanide ions to the environment is 0.5 mg/l a process had to be devised which was capable of both silver removal and destruction of toxic species to the desired levels. A process was developed which allows for the reduction of silver content of spent fixer from <5g/l to <0.5 mg/l so that the resulting effluent could be discharged directly to the streams. Silver is recovered as pure metal, no sludges are produced, and both biological oxygen demand and chemical oxygen demands are greatly reduced. The process involves the use of alkaline hypochlorite and hydrazine monohydrate through various steps that avoids the precipitation of $Ag_2S$ which is difficult to filter. This new process is now being scaled up for production operation. A patent application has been filed and additional research on the potential use of sodium dithionite in place of hydrazine is being investigated.

(Oak Ridge National Laboratory, F. Posey and A. Palko)

27. Mathematical Description Developed of the Transition of One Stable State of a System to Two Others Has Been Applied to Combustion Processes

Understanding the complex chemical and hydrodynamical effects occurring in combustion processes is important to the design of fuel-efficient and low pollution engines. Mathematicians at Northwestern University are analyzing the mathematical properties of the large systems of equations used to model combustion processes.

Theoretical studies on flame stability have generally been based on one of two approaches: (i) the Hydrodynamical model, which accounts for thermal expansion due to combustion but ignores flame structure and (ii) and diffusional-thermal model which considers flame structure in a prescribed constant density flow, thus ignoring thermal expansion. The Northwestern mathematicians derived a model in which both thermal expansion and flame structure are accounted for. They found that although plane flames are unstable to disturbances of very large wavelengths, as predicted by the Hydrodynamical model, there exists a critical wavelength below which plane flames may be stable, when diffusional-thermal effects are incorporated. The boundary between stability and instability is determined by the Lewis number, which is the ratio of thermal to mass diffusivities. When this ratio reaches a critical value, an unstable, cellularly shaped flame becomes a stable plane flame. This new, more rigorous mathematical model provides a much deeper understanding of the nature of the stability of flames.

The mathematics of combustion is vital to the understanding of experimental design and implementation, such as that carried out at the Combustion Research Facility at Sandia Livermore.

(Northwestern University, B. Matkowsky & Sandia Livermore, S. Margolis)

28. Computer Modeling Studies Support Concept of Using Heat Dervied from Magma Bodies to Convert Water -- Biomass Mixtures to Gaseous Fuels

Determining the scientific feasibility of tapping hitherto unavailable energy resources from the earth is an important objective of the BES Geosciences efforts in the program area of Resources Evaluation, Recognition and Utilization.

Studies conducted at the Sandia National Laboratories (SNL-A) have demonstrated that energy derived from magma could be used to generate higher quality fuels from biomass than direct use of the biomass itself as an energy source. It has been shown that the generation of gaseous fuels using biomass as the raw material can be achieved within a magma body, at the hot rock margins of the body, or at high temperature in surface reaction vessels with magmatically derived heat from a geothermal system.

The principal gas produced in the process is methane with hydrogen as a secondary fuel. The energy content of the gaseous fuels derived from the conversion process would be about 90 to 95% the energy content of the starting biomass material, which may be a low grade material such as pulp, agricultural waste, or other cellulose containing by-products. In addition, the ability to produce high quality geothermal steam at the same time would be only slightly reduced. Thus the process would make it possible to obtain a high quality fuel while at the same time producing steam for electric power generation or other uses, enhancing the economic value of exploiting geothermal energy sources.

(Sandia National Laboratories-Albuquerque, T. Gerlach)

29. Electrical Conductivity in Oil Shale During Retorting is Orders of Magnitude Different from that of Pre- or Post-retorted Material

Studies at the Lawrence Livermore National Laboratory have shown that the electrical conductivity of oil shale during retorting is a billion times greater than its value either before or after retorting. The high conductivity results from carbon migrating to grain boundaries during retorting. Because highly conductive material inside insulators can readily be detected with radiowaves, the retorting zone of an underground body of oil shale may be mapped remotely. Such remote mapping could be more cost-effective and interfere less with the retorting process than would thermocouples currently in use.

This new piece of fundamental information may also shed light on the question of abiogenic methane. Abiogenic methane, or methane formed from carbon and hydrogen deep within the earth's interior, unrelated to biological sources, has been proposed as a major potential source of energy. It is possible that the highly conductive layers in the earth's mantle could also be caused by carbon at grain boundaries. Such carbon, as it migrates toward the earth's surface, encounters water and could thus undergo reactions that produce methane. If such were the case, it would account for ther presence of abiogenic methane in the earth as a recent product rather than as a product left over from the time when the earth was formed from primordial matter.

(Lawrence Livermore National Laboratory, A. Duba)

30. New Pathway of Energy Conversion Using Inorganic Phosphorous as a Substrate Has Been Discovered

A new pathway of energy conversion using inorganic phosphorous as a substrate has been discovered in anaerobic bacteria. This finding has been substantiated in a number of different species of bacteria. The observation is that the microbes can use the energy of pyrophosphate to support growth when carbon compounds are available as building materials. Pyrophosphate was observed to stimulate growth of otherwise slow growing organisms. The finding may result in a way of enhancing reaction rates in anaerobic digestors and sewage treatment systems to produce methane gas.

(University of Georgia, H. Peck)

31. Adaptation of Plants to Water Submersion Stress

Deep water rice represents an unusual growth adaptation mechanism and recently the way in which the plant deals with the stress of flooding has become better understood. When floating rice plants are submerged, stress-ethylene synthesis is induced. Ethylene is a growth-promoting substance in floating rice varieties. The ethylene also accumulates in the hollow stems of the plant when it is submerged. Stress-induced ethylene synthesis and accumulation of ethylene in the tissue thus appear to be adaptive mechanisms. The capacity to produce ethylene and to react to it appear only after about four weeks of growth in air. This explains why floating rice varieties have to be pregrown on dry land for several weeks before they can cope with rising flood waters. It has also been discovered that floating rices have a mechanism to conduct air along their leaf surfaces to the plant parts below the water. Once these air channels are disturbed, the underwater parts of the plant become anaerobic, and they will not survive. This explains another empirical finding, namely that a short piece of the leaf must extend above the water for the plant to survive. Examination of the leaf surfaces reveals continuous air layers trapped between hydrophobic corrugated ridges. Most gas exchange is conducted through these external air layers. Non-flooding adapted plants have air layers many times smaller. In the dark, oxygen is actually pumped down through the air layers to support respiration and in the light the air layers facilitate $CO_2$ absorption from the water in support of photosynthesis in submerged portions of the plant. When leaves are treated with detergent the air layers are abolished and the leaves deteriorate when submerged. Work such as this on understanding fundamental adaptive mechanisms could lead to approaches for dealing with plant growth under adverse conditions.

(Michigan State University, H. Kende)

32. Water Soluble Product From Fungal Degradation Not Previously Observed Has Been Isolated

A water soluble product from the fungal (Streptomyces) degradation of lignin has recently been isolated which is called acid precipitable polymeric lignin. The product can be recovered as more than 30% of the original total lignin. This product has not been observed previously and could serve as a potentially valuable industrial chemical for use as an adhesive or coating. A patent for this product is pending and there is interest on the part of industry.

(University of Idaho, D. Crawford)

33. Extension of Vibrational Control Theory to Operation of Catalytic Reactors

Very often the energy efficient production of various useful chemical compounds is limited by the occurrence of instabilities. These instabilities may cause the chemical process either to quench itself, thus ceasing the production; or to bring about explosive, hazardous conditions. The prevention of either extreme, while increasing the potential chemical product output is an important problem in the control of chemical reactors which is addressed at the Illinois Institute of Technology, Chicago, Illinois.

Recent advances in vibrational control theory showed how high frequency pulsations of the reactor temperature can increase the region of parameters in which stable catalytic reactor operation is obtained. This implies of course that the yield of such reactors may be significantly improved. In addition computer simulations of the operation of catalytic reactors revealed that relatively low frequency temperature oscillations also increase significantly the region of stability. This has both practical and theoretical importance. In practice varying temperatures slowly is accomplished more readily and less expensively than changing it at a high rate. From the broad theoretical point of view low frequency vibrational control in general appears to be a relatively new and unexplored concept with potentially important consequences for control engineering.

It is expected that the new results will eventually impact positively on chemical industrial practice by permitting process which produce chemicals at a lower energy consumption rate. Furthermore, the discovery of low frequency vibrational control should open the doors to possible new control techniques.

(Illinois Institute of Technology, S. M. Meerkov)

## 34. Instrumentation Developed and Demonstrated for Detection of Internal Cracks in Large Structures

Small, nearly microscopic cracks in a structure are potential precursors of a failure of the structure. Such a fracture may reach catastrophic proportions in energy-related structures, e.g., nuclear reactors, high pressure boilers, nuclear waste containers and the like. Early detection of such minute cracks presents a serious instrumentation problem which is addressed in several places, notably Ames Laboratory, Ames, Iowa.

Recent advances in the instrumentation for non-destructive evaluations permit for the first time the detection and characterization of cracks the size of a hair in many important structures. The new method features a unique combination of 1) a novel configuration of advanced high-frequency sound generators and detectors (ultrasonic transducers), 2) recent advances in theories of acoustic scattering, and 3) ingenious data processing techniques. This type of instrumentation will permit a rapid detection of cracks as small as two thousandths of an inch. It will also signal the location, dimensions and relative orientation of the cracks; information which is essential for predicting the future growth of the cracks.

The application of this new technique is expected to lead to improved assurance of fitness for service and safety of many energy-related structures.

(Ames Laboratory, J. Corones, D. O. Thompson and R. B. Thompson)

## 35. Have We Seen a $CO_2$ Warming?

A working consensus has been reached that it is not yet possible to detect the warming expected from past growth of atmospheric $CO_2$.

Several diagnostic studies have attempted to isolate the $CO_2$ warming signal in the 100 year temperature record subtracting out other possible signals. Almost all studies have "seen" a $CO_2$ signal. However, each investigator reduced the "noise" in their own way and several derived their own temperature record. The noise reduction techniques are even in conflict. For example, one researcher requires a measure of solar variability and volcanism to isolate a signal, while another requires only volcanism and tropospheric dust to isolate a signal. Further, some key features of the data set are difficult to "fit". For example, one analysis fits the overall trend in the northern hemisphere record well, but the model does not reproduce the 1960-1975 cooling. Establishing this consensus among leaders in the field has been an important step in defining both research needs and a viable research plan.

(Lawrence Livermore National Laboratory, M. C. MacCracken)

36. Capabilities, Limitations and Prospects - Simulating $CO_2$-Induced Climate Change

It appears premature to draw firm, detailed conclusions from the available climate model simulations of $CO_2$-induced climate change. This result is based on research analyzing the capabilities, limitations and prospects of mathematical climate models. The analysis compares, primarily the General Circulation Models (GCMs) on temperature, precipitation-rate and soild moisture. These comparisons reveal similarities and differences among the GCM simulations, and some possible explanations for these differences. The models differ in their geography/orography, ocean models and solar forcing, and because, for the simulations which can be rigorously compared, either equilibrium has not been reached, or the simulated climate changes are not all statistically significant between runs within the same model. These results go beyond the recent National Academy of Sciences study in technical detail and implications for future research.

(Oregon State University, M. C. Schlesinger)