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Final Report

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EXPLORATORY BASIC ENERGY RESEARCH
CONDUCTED AT STANFORD UNIVERSITY
IN THE PERIOD
SEPTEMBER, 1979-AUGUST, 1983

Under support of the

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Administered through the
Stanford Institute for Energy Studies
W. C. Reynolds, Principal Investigator

January, 1984

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I. INTRODUCTION

The Institute for Energy Studies (IES) was formed at Stanford in 1974 under the chairmanship of Professor W. C. Reynolds. The principal mission of the IES is to assist faculty in developing new energy-related research programs. Support for the Institute comes principally from industrial gifts, which are generally unrestricted and hence can be deployed for high-risk, high-payoff preliminary research.

In September, 1978, the Department of Energy awarded a contract to Stanford for Exploratory Basic Research. Projects to be supported were to be chosen by Stanford, with emphasis being placed on exploratory research likely to lead to full-scale research programs under support of appropriate agencies.

Funding was provided for three years, as follows:

FY79	\$150K
FY80	200K
FY81	<u>250K</u>
	\$600K

The actual expenditures were extended over a four-year period. Table 1 shows the expenditure summary, based on Stanford's academic year of Sept. 1-Aug. 31.

The DOE funds provided through this contract were used, in combination with the IES industrial funds, to support exploratory basic energy research in three ways:

- (1) Funding of faculty members for the initial phases of research. Most of the funding was used in this manner.
- (2) Support of the Energy Information Center, a small special document center that holds information pertinent to energy research, both as related to energy policy and energy technology and to the supporting basic sciences. Approximately 12% of the funding was used in this manner.
- (3) Through support for seminars, occasional visitors, and program administration. Approximately 6% of the funding was used for this general support of the energy ambiance at Stanford.

Table 1

SUMMARY OF EXPENDITURES
(Thousands of Dollars)

Academic Year	Salaries & Benefits	Equipment	Supplies	Total Direct Expense	Indirect Expense	Total
1979	16	45	9	70	15	85
1980	22	86	6	114	16	130
1981	45	88	25	158	41	199
1982	52	25	19	96	40	136
1983	18	1	13	32	18	50
Totals	153	245	72	470	130	600

II. PROGRAM ELEMENTS

1. Exploratory Research

The exploratory research funds provided by the DOE grant were leveraged by combination with industrial funds; overall, the DOE and industrial dollars spend in exploratory research were approximately equal, though the allocation of each varied from project to project. Only projects supported under this contract are reported here. For overviews on other energy research at Stanford, see the accompanying book Energy Research at Stanford (1982).

Brief proposals from individual faculty members were received by the IES chairman and reviewed by others with expertise relating to the proposed area. Factors considered in deciding which projects to support were:

- The importance of the proposed work.
- The past performance record of the investigator.
- The likelihood that the research would develop into a major research program capable of generating its own research support.

Support in the range \$10-50K for six months to one year was typical. Practically all of the exploratory projects led to formal agency research proposals, and most of these were funded by the DOE, EPRI, NSF, or other appropriate agencies.

The exploratory funding generally provided equipment, support for students and professional research staff, supplies, and in some special cases travel, but as a rule did not include faculty salaries. As a result, the overall allocation for equipment was high in comparison to most sponsored projects, and consequently the indirect costs were kept well below the average for engineering and science research contracts. This maximized the impact of the DOE funding (see Table 1).

Table 2 summarizes the research projects supported. They have been grouped into four areas, but several could be put in more than one area.

Included on this table is the reported research expenditure for the academic year ending August, 1983, for each of the investigators involved in the exploratory research program. Since it is difficult to be precise in tracking sponsored research to its exploratory genesis, all research guided by each investigator has been included, but some large programs have been omitted

(e.g., Bienenstock's \$5000K Synchrotron Radiation Project and Kruger's \$650K MHD and plasma research).

After reviewing the work of several of these investigators, it seems safe to say that a large fraction of the work listed as "post-exploratory" was either a direct follow-on of the exploratory research or was significantly influenced by it. The high percentage of projects sponsored by the Department of Energy and its National Laboratories (LBL, SNL, LLL, SERI) and the Electric Power Research Institute attests to this claim.

The numbers suggest that the leverage on exploratory research funding is about a factor of 10. That is, a successful exploratory research effort funded at \$20K for one year generates an agency-supported specific research program at the level of \$100-200K per year that will extend over several years. This clearly indicates the value of the exploratory work in helping to define the research area before a more formal proposal is submitted. A consequence of this certainly is better quality in the research conducted over the long run, and hence high payoff for the agencies in terms of the rate at which significant advances are made.

As a matter of policy, research at Stanford is conducted as part of the training of doctoral students, and projects that do not involve students generally are not approved. Thus, the projects listed on Table 2 involved on the order of 20 doctoral students. Through their impact on other research of the faculty-student research teams, these exploratory projects indirectly affected many more students. The successful agency proposals that were produced as a result of the exploratory funding probably involve upwards of 50 doctoral students. Hence, in addition to having a very significant impact on the research mission of the university, this exploratory research funding contributed to the educational mission in a significant way.

The overall impact of the Institute for Energy Studies, and this DOE exploratory research program in particular, in increasing the energy-related research activity at Stanford was very significant. However, it was not a case of providing research funding for otherwise dormant faculty. Rather, it provided a key mechanism for the redirection of the efforts of some of Stanford's most productive scholars to problems of direct importance to the Department of Energy. Indeed, without the impetus for redirection that the exploratory research funds provided, it is unlikely that very many of these

Table 2

SUMMARY OF PROJECTS SUPPORTED

Area	Project Number	Faculty Investigator	Project	Exploratory Funding	Post-exploratory Funding AY 1982-83 ^{††}	Supporting Agencies
A. <u>Solar</u>						
	1	Bienenstock	Amorphous Silicon	\$20K	\$160K ^{**}	NSF, DOE
	2	Brown	Silicon Fabrication	23K	160K	NSF
	3	Boxer	Artificial Photosynthesis	30K	82K	NSF
	4	Bube	Thin-film Junctions	6K	404K	DOE, SERI
	5	Seigman	Semiconductors	5K	40K	DOE
B. <u>Geothermal</u>						
	6	Mahood	Volcanic Diagnostics	18K	29K	NSF
C. <u>Fossil</u>						
	7	Beyer	Combustion Diagnostics	51K	70K	LLL, AFOSR
	8	Collman	Catalysis	14K	171K	NSF
	9	Eaton	Fluidized Beds	10K	15K	Industry
	10	Eustis	Energy Systems Analysis	10K	180K ^{††}	DOE, EPRI
	11	Hanson	Combustion	15K	500K	DOE, NSF, AFOSR
	12	Huggins	Coal Fuel Cell	65K	380K ^{††}	LBL, SNL
	13	Kruger	Coal Combustion	55K	150K ^{††}	DOE, EPRI
	14	Laurman	CO ₂ Impact	10K	--	--
	15	Madix	Catalysis	15K	150K	DOE, NSF
	16	Matin	Microbial Desulfurization	15K	--	--
	17	Quate	Acoustic Diagnostics of Coal	40K	180K	ONR
	18	Reynolds	I.C. Engine Flows	10K	10K	Industry
D. <u>Materials</u>						
	19	Fuller	Polymer Mechanics	10K	150K	NSF
	20	Miller	High-Temperature Deformation	10K	305K	DOE, EPRI
	21	Herrmann	Damage Mechanics	20K	133K	DOE, ONR
E. <u>Energy Policy</u>						
	22	Manne, Sweeney	Energy Modeling	\$10K	550K	DOE, EPRI, GRI, Industry
				\$462K		
F. <u>Energy Information Center</u>						
				98K		
G. <u>General Administration and Minor Project Assistance</u>						
				\$40K		
Grand Total:				\$600K		

*Dollar figures are approximate.

[†]Based on actual expenditures for year ending Aug. 31, 1983, investigators' research contracts/grants.

^{**}Does not include research supported through DOE-funded \$5000K/yr SSRP project.

^{††}Does not include the Stanford MHD program supported by DOE/EPRI at \$600K/yr.

investigators would have turned away from their secure funding from other sources to work on energy-related research.

Details on the projects supported under the DOE contract are included in the Appendix.

2. Energy Information Center

The Energy Information Center (EIC) is a special document center containing a great deal of current information vital to energy research. It has a full-time librarian who has some part-time student assistance. The collection is continually revolving and expanding, and contains several thousand items at any one time.

Typical collection items are journals of energy research, interim reports from various energy sub-committees, working reports from energy research projects being conducted elsewhere, current energy supply and use statistics, and industrial reports describing advances in energy technology. The EIC collection is especially useful for research on matters of energy policy, and has been widely used by the Stanford community. It has also been used by the staff of local congressmen, EPRI, the California Energy Commission, and Bay Area energy companies.

Support for the EIC through the DOE contract was matched with IES industrial funds.

3. Administration

During the period of the contract, the IES was administered by Prof. W. C. Reynolds, then IES Chairman and Chairman of Mechanical Engineering. A portion of his salary and that of the IES secretary was charged to the DOE contract. Minor amounts were also used to support speakers at energy-related research seminars, to provide travel for research development, and in other ways that help maintain a strong energy thrust at Stanford.

III. RECOMMENDATIONS

We believe that this program of exploratory research was extremely successful in terms of the stimulation it provided for new research. Therefore, we recommend that this type of program be maintained at the leading research universities, where there is much talent to bring to bear on the problem areas addressed by the Department of Energy.

Most investigators found that special equipment was the key to new exploratory research, attesting to the importance of equipment-grant programs. Equipment grants are important not only for large facilities, such as accelerators, but also for smaller, dedicated instruments for individual investigators. An instrument cost in the range \$30-\$50 generally is too large for individual grants or contracts to carry and too small for the major federal instrumentation programs. Therefore, we recommend that the Department of Energy take special steps to provide additional support for research instrumentation, especially to meet the needs of individual investigators.

At the leading research universities, this type of exploratory research should be done using matching-funding concepts, such as employed by the Institute for Energy Studies. This procedure serves to identify seriously considered needs. And, because industry assists university those groups that produce effective research and graduate students, it helps to ensure that the groups so supported are ones who will use the equipment well.

APPENDIX

BRIEF PROJECT DESCRIPTIONS

1. ELECTRON-HOLE RECOMBINATION IN AMORPHOUS SILICON

Investigator: Professor A. Bienenstock
Department of Materials Science and Engineering

Exploratory Research Funding: \$20K

Project Description:

The investigation has developed an experimental system at the Stanford Synchrotron Radiation Laboratory (SSRL) in which synchrotron radiation is used to study time-resolved photoluminescence (PL) from amorphous semiconductors. The material of particular interest is a-Si:H, as this material has been shown to demonstrate the characteristics required for photovoltaic applications when appropriately prepared. That is, its relatively low density of states in the pseudogap permits doping to produce n- and p-type material.

Time-resolved PL allows examination of the nature of recombination in an amorphous semiconductor and identification of the defect states and impurities responsible for depleting the population of free carriers in a photovoltaic device. In particular, the investigator studied the effect of a static magnetic field on the PL intensity as a function of time. This study yields a measure of the electron-hole correlation throughout the recombination process and will determine the extent of "geminate recombination" in a-Si:H. Geminate recombination is the case where the conduction electron and hole never separate throughout their lifetimes. They cannot contribute to the conduction of current in a photovoltaic device and thus represent wasted energy in the energy-conversion process.

The exploratory research funding enabled the investigator to purchase a special photomultiplier tube that allows detection of PL radiation in the near-IR (greater than 1.1 eV), and a helium cryostat that gives the capability to vary the temperature of the experiment down to 1.5°K. Two characteristics of synchrotron radiation make this experimental system exceptional. First, the pulsed time structure of the radiation yields very sharp excitation pulses only several hundred picoseconds wide. These pulses, for the first time, allow study of amorphous semiconductor PL lifetimes down to one nanosecond. In addition, one is able to vary the excitation energy continuously from 1.0 to approximately 5 eV, due to the tunability of the synchrotron radiation. Finally, integrating an acousto-optic modulator into the system will cyclicly extract a single pulse of synchrotron radiation and then reject an arbitrary number which follow. In this way, one can measure PL lifetimes that are longer than the 780 nanosecond time between synchrotron radiation pulses at SSRL.

The continuing work in this area is now supported by the National Science Foundation and by the Department of Energy through the Stanford Synchrotron Radiation Project, which provides his students with a unique basis for their doctorate education.

2. PROPERTIES OF SOLAR-CELL PURITY SILICON MELTS

Investigator: Professor Gordon E. Brown, Jr.

Exploratory Research Funding: \$25K

Project Description:

A very promising process for electrodepositing silicon metal from high-temperature silicate melts was discovered by the crystal growth group (Feigelson, Elwell, and DeMattei) of the Stanford Center for Materials Research (CMR). However, their initial trial runs showed that silicate melts of certain compositions yielded no metallic silicon at the cathode, even though these melts were of low viscosity and high conductivity, two conditions found empirically to be necessary for electrodeposition to occur. Their most successful results were obtained for low-viscosity melts in the system $\text{BaO-BaF}_2\text{-SiO}_2$, from which they achieved a 15-22% efficiency of silicon deposition.

The objective in this exploratory project was to gain a fundamental understanding of the dependence of viscosity on the short-range structure of alkali and alkaline-earth silicate melts in order to suggest possible ways of improving the efficiency of the electro-winning process and of separating the silicon metal produced from the melt. The initial work was directed towards an analysis of available transport data on the $\text{BaO-BaF}_2\text{-SiO}_2$ system and the measurement of additional transport data.

The investigator also spent fruitful time with Dr. Elwell of CMR visiting the silicon electrodeposition laboratory and discussing their experimental results. These discussions indicated that efficiency of electrodeposition in the $\text{BaO-BaF}_2\text{-SiO}_2$ system could be improved by ensuring that compositions not fall in the two-liquid region of this system. Loss of Ba from their melts due to volatilization of this element could easily shift the melt composition into the two-liquid field, resulting in phase separation of the melt and rather drastic changes in transport properties. Such loss could also shift the system composition so that the nearby liquidus boundary is intersected, resulting in partial crystallization of the melt. This effect would also hinder the electrodeposition process by increasing the effective viscosity and decreasing the diffusion rates and electrical conductance of the melt.

Viscosities of selected alkali and alkaline-earth melts were measured using a rotating cup viscometer at Lawrence Livermore Laboratories. Several experiments on BaO-SiO_2 melts duplicated the existing viscosity data in the literature (Bockris et al., 1955; Trans. Faraday Soc., 51, 1734-1748). Addition of BaF_2 to these melts reduced their viscosities below 1500 poise, which is the lower limit of measurement for the viscometer system available for these experiments. A series of viscosity measurements were initiated in the $\text{Na}_2\text{O-SiO}_2$ and $\text{Na}_2\text{O-Al}_2\text{O}_3\text{-SiO}_2$ systems.

Work on the $\text{Na}_2\text{O-Al}_2\text{O}_3\text{-SiO}_2$ system resulted in measurements of viscosity changes due to partial crystallization of the melt. Therefore, observations in this system are of use in understanding and modeling the expected

changes in viscosity as crystallization occurs in the $\text{BaO-BaF}_2\text{-SiO}_2$ system or as silicon metal is separated from the melts during electrodeposition. In either case, the viscosity of the melt will change. Relative viscosity increases markedly as the volume concentration of particles increases. The silicon metal in $\text{BaO-BaF}_2\text{-SiO}_2$ melts was found to separate as small, roughly spherical globules up to about 2 mm in diameter (Elwell, personal communication, 1981). The presence of such particles can change the melt viscosity up to several orders of magnitude as their volume fraction increases from a few percent up to 10-20% of the melt. The viscosity increase will reduce the efficiency of the electrodeposition process. Therefore, it is critical that the particles be removed in order to enhance electro-winning efficiency.

Removal of the silicon metal particles from the melt has proven to be the most difficult problem in the electro-winning of silicon, because the silicon floats just below the melt surface. Thus, mechanical separation is virtually impossible. Several solutions to this problem are possible, based on a study of available literature on the properties of silicate minerals and melts. Inclusion of small amounts of GeO_2 in the original melt will result in an increase in the average density of the melt, causing a greater density contrast between the silicon metal globules and the melt. If the contrast is high enough, the silicon metal particles may float at the surface, from which they could be mechanically removed. Substitution of Ge for Si in the melt should not affect the short-range melt structure, the melt viscosity, or the photovoltaic properties of the separated silicon metal. A second possible solution to the separation problem might involve the addition of Al_2O_3 to the $\text{BaO-BaF}_2\text{-SiO}_2$ system. Al substitutes readily for Si in minerals and melts, so long as sufficient alkaline-earth or alkali metal cations are present for local charge balance. The overall effect of adding Al_2O_3 would be to reduce the average density of the melt as well as its viscosity. As in the case of addition of GeO_2 , the enhanced density contrast between the separated silicon metal and melt might result in a sinking of the metal globules, making possible a gravity separation.

A second priority in this exploratory project was to establish a laboratory for X-ray radial distribution analysis of high-temperature melts. This facility permits the direct study of short-range structure of melts in the system $\text{BaO-BaF}_2\text{-SiO}_2$, as well as other systems below about 1600°C. The investigator visited the X-ray laboratory of Dr. C. N. J. Wagner at UCLA for the purpose of examining his energy-dispersive melt diffractometer. A Phillips 100 kV X-ray generator and an intrinsic germanium detector system were obtained and a graphite furnace constructed. This new QMR laboratory will be of great usefulness in structural characterization of silicate and metallic melts; it will also be of value in the QMR thrust program on metallic glasses.

The continuing work of the investigator and his students is now supported by the National Science Foundation.

3. NATURAL AND ARTIFICIAL PHOTOSYNTHESIS

Investigator: Professor Steven Boxer
Department of Chemistry

Exploratory Research Funding: \$30K

Project Description:

Natural photosynthesis provides a useful model for solar-energy collection, transport, charge separation, and chemical synthesis. This project focuses on collection, transport, and charge separation.

Chromophore arrays are expected to serve as light "antennas" in synthetic photosynthetic systems, much as they do in natural systems. The exploratory research funding led to the fabrication of the first well-defined monomeric 1:1 chlorophyll-protein complex. This complex is ideally suited for studies of chlorophyll-mediated energy transport, because the chromophores are insulated from each other by the protein, which prevents chromophore aggregation. The proteins form well-characterized aggregates (dimers and tetramers) which precisely position the chromophores in three dimensions relative to each other. The proteins also form single crystals of exceptional optical quality whose structure has been determined by X-ray analysis. These crystals have been used to establish the orientations of a number of chlorophyll spectroscopic properties. This is the key information needed to analyze the structure of natural reaction centers.

Time-resolved fluorescence techniques have been developed to study energy migration in these systems on a picosecond time scale. The investigator perfected a fluorescence system at the Stanford Synchrotron Radiation Laboratory which permits fluorescence lifetime and anisotropy measurements on the time scale of 50 ps or longer, with excitation and detection at any wave-length in the near-UV to near-IR. This technique and ps sum-generation methods developed in Professor Fayer's laboratory have been applied to study energy transport and trapping in these well-defined systems. This provides the parameters which are needed to optimize energy transport in artificial molecular solar collectors.

The investigator discovered that the yields of photosynthetic intermediates can be directly influenced by strong magnetic fields. The physical principles and theory have been worked out in detail, leading to a new method for studying charge separation in solids (this will be of general interest for studying solar-energy-related materials). The investigator also discovered that these effects are highly anisotropic. This discovery leads to information on the orientations of electron donors and acceptors in the solid state. Analysis of the temperature dependence of these effects provides information on the relative energies of intermediates. This is a key piece of information in estimating photosynthetic efficiency and in determining the optimal energetics for artificial photosynthetic systems.

Several approaches have been explored for duplicating photosynthesis in entirely artificial systems. This has included the synthesis of covalently

connected donors and acceptors, followed by spectroscopic studies of the efficiency of charge separation. Recent work has been focused on the construction of unique molecular environments for electron transfer using proteins and synthetic molecules.

The exploratory research funding provided the equipment needed for this young investigator to start his research program at Stanford. It is now supported by the National Science Foundation, the Gas Research Institute, and the U. S. Department of Agriculture at a level of approximately \$230,000 per year, and has been extremely productive in both research and Ph.D. training.

Selected Publications

- S. G. Boxer and R. R. Bucks, "A Structural Model for the Photosynthetic Reaction Center," Journal of the American Chemical Society, 101, 1883-1885 (1979).
- S. G. Boxer and K. A. Wright, "Solution Properties of Synthetic Chlorophyllide- and Bacteriochlorophyllide-Apomyoglobin Complexes," Biochemistry 10, 259-264 (1981).
- R. R. Bucks and S. G. Boxer, "Synthesis and Spectroscopic Properties of a Novel Cofacial Chlorophyll-Based Dimer," Journal of the American Chemical Society, 104, 340-343 (1982).
- S. G. Boxer, C.E.D. Chidsey, and M. D. Roelofs, "The Use of Large Magnetic Fields to Probe Photoinduced Electron Transfer Reactions: An Example from Photosynthetic Reaction Centers," The Journal of the American Chemical Society, 104, 1452-1454 (1982).
- S. G. Boxer, C.E.D. Chidsey, and M. D. Roelofs, "Dependence of the Yield of a Radical Pair Reaction in the Solid State on Orientation in a Magnetic Field," The Journal of the American Chemical Society, 104, 2674-2675 (1982).
- R. R. Bucks, I. Fujita, T. L. Netzel, and S. G. Boxer, "A Picosecond Spectroscopic Study of Chlorophyll-Based Models for the Primary Photochemistry of Photosynthesis," The Journal of Physical Chemistry, 86, 1947-1955 (1982).
- S. G. Boxer, C.E.D. Chidsey, and M. G. Roelofs, "Anisotropic Magnetic Interactions in the Primary Radical-Ion Pair in Photosynthetic Reaction Centers," Proceedings of the National Academy of Sciences, USA, 79, 4632-4636 (1982).
- A. Kuki and S. G. Boxer, "Chlorophyll-Substituted Hemoglobin Tetramers and Hybrids: Preparation, Properties and Energy Transfer," Biochemistry, 22, 2923-2933 (1983).
- S. G. Boxer, C.E.D. Chidsey, and M. G. Roelofs, "Magnetic Field Effects in Solid-State Photochemistry and Spectroscopy," Annual Review of Physical Chemistry, 34, 390-417 (1983).

4. THIN-FILM SOLAR CELL RESEARCH

Investigator: Professor R. H. Bube
Department of Materials Sciences and Engineering

Exploratory Research Funding: \$6K

project Description:

The investigator and his students are heavily involved in thin-film solar cell research. The exploratory research funding enabled him to obtain a vacuum deposition system, which is now in use in his program.

Particular attention involves heterojunctions in which the optically active p-type member is CdTe, which is a near-ideal bandgap for solar energy conversion. Research involves single-crystal CdTe and thin-film CdTe deposited by close-spaced vapor transport. High-resolution-transmission electron microscopy is included for physical information on interfaces.

Photovoltaic heterojunctions consisting of CdS/CdTe, ZnCdS/CdTe, ITO/CdTe, and ZnO/CdTe have been prepared using vacuum evaporation, spray pyrolysis, sputtering, and electron-beam evaporation of the large bandgap window material on the CdTe. Highest efficiency achieved to date is 10.5 percent on an ITO/CdTe heterojunction with ITO deposited by electron beam evaporation on single-crystal CdTe. A major advance has been made with the high-resolution transmission electron microscopy imaging of the first electrically characterized solar cells: CdS/CdTe cells formed by vacuum evaporation of CdS on single-crystal CdTe.

In another part of his program, the investigator and his students seek to carry out two distinguishable and yet closely related tasks: (1) the preparation of thin-film CdTe using hot-wall evaporation methods, and (2) the preparation and analysis of single-crystal CdTe, especially with regard to grain boundary properties in bicrystals.

The two avenues of research mentioned above are combined by a comparison of the electrical, optical, and structural properties of the two forms of CdTe, together with an analysis of the properties of various Schottky barriers, heterojunctions, or other junctions formed using them. Information on properties and passivation of grain boundaries will be applied to the thin films of CdTe. Final goal is the development of an all thin-film CdTe solar cell.

A variety of n-type CdTe thin films have been prepared to date, and the correlation between preparation conditions and final electrical and optical properties has been determined. Schottky barrier or MIS junction structures are being prepared on these films. The deposition of p-type CdTe films has been achieved, with all thin-film solar cell performance being informed also by the research on grain boundary properties and passivation.

Professor Bube's work in this area is currently supported by the Department of Energy and the Solar Energy Research Institute.

Selected Publications

- F-C. Wang, A. L. Fahrenbruch, and R. H. Bube, "Transport Mechanisms for $\text{MG/Zn}_3\text{P}_2$ Junctions," J. Appl. Phys., **52**, 8874 (1982).
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- A. L. Fahrenbruch and R. H. Bube, Fundamentals of Solar Cells, Academic Press, New York (1983).
- W. Huber, A. L. Fahrenbruch, C. Fortmann, and R. H. Bube, "Grain Boundary Phenomena in n-type CdTe Films Grown by Hot Wall Vacuum Evaporation," J. Appl. Phys., **54**, 4038 (1983).
- J-P. Häring, A. L. Fahrenbruch, and R. H. Bube, "Effects of Surface Preparation on the Properties of Metal/CdTe Junctions," J. Appl. Phys., **54**, 4982 (1983).
- T. Yamashita, J. G. Werthen, R. H. Bube, and R. Sinclair, "Lattice Imaging of CdS/CdTe Solar Cell Interface," Proc. 41st Ann. Meeting of the EMSA, (G. W. Bailey, ed.), San Francisco Press (1982), p. 124.
- J. G. Werthen, J-P. Häring, A. L. Fahrenbruch, and R. H. Bube, "Surface Effects on Metal/CdTe Junctions and CdTe Heterojunctions," J. Phys. D: Appl. Phys., **16**, 239 (1983).
- C-T. Lee and R. H. Bube, "Low-Resistance Contacts to p-type Li-Diffused CdTe," J. Appl. Phys., **54**, 7041 (1983).

5. PICOSECOND STUDIES IN SEMICONDUCTORS

Investigator: Professor A. E. Siegman
Department of Electrical Engineering

Exploratory Funding: \$5K

Project Description:

Professor Siegman and his students work in the area of ultra-fast electronics sciences. The exploratory research funding enabled him to assemble a laser diagnostic system for study of thin-film solar cell materials developed by Prof. Bube, as well as other technologically important semiconductors. This technique uses picosecond optical pulses to study ultrafast relaxation and transport phenomena in crystalline and amorphous semiconductors and to produce and study phase transitions in various solids.

Mobility and lifetime as a function of time, with better than 100 psec time resolution, are being measured in thin film of silicon ($\sim 1/2 \mu\text{m}$ thick) on quartz or glass and in thick films of crystalline or ion-implanted Si and GaAs. The films are either amorphous or polycrystalline, with grain size between $1000\text{\AA}$ and $40 \mu\text{m}$. The techniques used to make these measurements are the transient grating method [1] and the two-color excitation technique [2-4], both of which have been developed in his laboratory. The laser source is a Q-switched and mode-locked Nd:YAG laser system, operating at either $1.06 \mu\text{m}$ or 532 nm . Understanding the dynamics of these semiconductor samples on a picosecond time scale is relevant to the solar energy effort and is of crucial importance for the integrated circuit technology, since for example a lot of effort is spent in making fast circuits in these thin films.

A general study has been undertaken of the various phase transitions that can occur at semiconductor and metal surfaces during illumination by ultra-short, high-power laser pulses [5-11]. This effort, initially directed toward a better understanding of the pulsed-laser annealing phenomenon in ion-implanted silicon, has been extended to a study of various transitions (amorphous $\rightarrow$ polycrystalline, crystalline $\rightarrow$ amorphous, damage, etc.) at the surface of Si, GaAs, and Cu. The conditions for the creation of spontaneous periodic surface structures in these materials [5-9] and in the effect of repetitive laser illumination have been specially investigated [5-11]. Real-time experiments also are performed to better understand the dynamics of surface phase transitions. This research is clearly important to the semiconductor industry, since laser annealing has established itself as a useful technique for removing damage in ion-implanted semiconductors, and since ultra-short, high-power laser pulses can induce locally some transitions that cannot be obtained by other means. In addition, the physics of these various laser-induced transformations is of scientific interest (they involve material's responses of the order of one picosecond, a poorly known regime).

This work is now supported by a variety of agencies, including the Department of Energy. One student working on this project has already obtained his Ph.D., and several other students are or have been in part associated with this project.

Selected Publications

1. J. R. Salcedo et al., "Dynamics of Energy Transport in Molecular Crystals: The Picosecond Transient Grating Method," Physical Review Letters, **41**, 131 (1978).
2. P. M. Fauchet and A. E. Siegman, "Evidence for a Dense Electron-hole Plasma Close to the Melting Phase Transition in Silicon," Applied Physics Letters, **43**, 1043 (1983).
3. P. M. Fauchet and A. E. Siegman, "Two-color Picosecond Measurements on Electron-hole Plasmas Close to the Melting Phase Transition," to be published in Energy Beam-Solid Interactions and Transient Thermal Processing (Fan and Johnson, eds.), North-Holland (1984).
4. P. M. Fauchet and A. E. Siegman, "Picosecond Dynamics of Electron-hole Plasmas Close to the Melting Phase Transition in Silicon and Gallium Arsenide," to be published in the Proceedings of the International Conference on Lasers '83 (1984).
5. P. M. Fauchet and A. E. Siegman, "Surface Ripples on Silicon and Gallium Arsenide under Picosecond Laser Illumination," Applied Physics Letters, **40**, 824 (1982).
6. P. M. Fauchet and A. E. Siegman, "Spontaneous Surface Ripples on Semiconductors under Picosecond Laser Illumination," paper presented at CLEO Conference, Phoenix, AZ, April 1982, WK6.
7. P. M. Fauchet, G. Zhou, and A. E. Siegman, "Periodic Ripple Structures on Semiconductors under Picosecond Pulse Illumination," paper presented at 3rd Topical Meeting on Picosecond Phenomena, Garmisch-Partenkirchen, June 1982, TB6.
8. G. Zhou, P. M. Fauchet, and A. E. Siegman, "Growth of Spontaneous Periodic Surface Structures on Solids during Laser Illumination," Physical Review B **26**, 5366 (1982).
9. P. M. Fauchet, G. Zhou, and A. E. Siegman, "Picosecond Laser-induced Surface Transitions in Solids," in Laser-Solid Interactions and Transient Thermal Processing of Materials, (Narayan, Brown, and Lemons, eds.), North-Holland, 1983, p. 205.
10. P. M. Fauchet, "Gradual Surface Transitions on Semiconductors Induced by Multiple Picosecond Laser Pulses," Physics Letters, **93A**, 155 (1983).
11. P. M. Fauchet and A. E. Siegman, "Observations of Higher-order Laser-induced Surface Ripples on <111> Germanium," Applied Physics, **A32**, 1983, 135 (1983).
12. P. M. Fauchet, "The Auger Rate in Highly Excited Indium Antimonide," Physica Status Solidi b, **110**, K11 (1982).
13. A. E. Siegman, "Developments in Mode-locked Lasers and Their Applications," Proceedings of the Society of Photo-Optical Instrumentation Engineers, **322**, 1982.

6. DIAGNOSTICS OF VOLCANIC MATERIALS

Investigator: Professor Gail Mahood
Department of Geology

Exploratory Research Funding: \$18K

Project Description:

The exploratory research funding enabled the construction of a special diagnostic line for measuring the K-Ar content of volcanic materials. This extraction line is specifically designed for the dating of young volcanic rocks. Precise and accurate dating of eruptive units less than one million years old is important in estimating the age and recurrence rates of active faults, in assessing volcanic hazards, and in estimating the potential of geothermal areas associated with young volcanic activity.

The extraction line was assembled, enabling the investigator to make these unique measurements. Subsequently, her work has been supported by the National Science Foundation.

7. LASER TOMOGRAPHY FOR COMBUSTION DIAGNOSTICS

Investigator: Professor R. L. Byer
Department of Applied Physics

Exploratory Research Funding: \$51K

Project Description:

The goal of this research program is to make measurements of combustion processes using new and advanced laser methods. The investigator is one of the leading developers of tomography as a method of obtaining two-dimensional species concentration measurements in flames.

Work under the exploratory funding centered on modeling studies of laser tomography. The investigator and his students completed a detailed study of the sensitivity, signal-to-noise, and geometry of laser tomography. This work shows very clearly that laser tomography will provide a unique and very sensitive new measurement method.

Based on the results of the modeling study, the exploratory research funds were used to initiate an experimental effort to demonstrate laser tomography. This machine allows reconstruction of the tomogram image in approximately 20 minutes and display of the image on a high-resolution graphics monitor.

The investigator also considered methods of introducing and sampling optical radiation into combustion chambers via single-crystal sapphire fibers. The advantages of the fibers are high melting point, good mechanical strength, and high optical transmittance from 0.2-6.0 μm . He and his students are now developing sapphire fibers to implement laser tomography in real combustors, including research on internal combustion engines.

This work is now supported by the Air Force Office of Scientific Research as part of its extensive combustion diagnostics program.

Selected Publications

- R. L. Byer and L. A. Shepp, "Two-Dimensional Remote Air Pollution Monitoring via Tomography," Optics Letters, **4**, 75 (March 1979).
- D. C. Wolfe, Jr., "On the Application of Optically Computed Tomography to Remote Air-Pollution Measurement," Ph.D. dissertation, Stanford University, June 1980.
- D. C. Wolfe, Jr., and R. L. Byer, "Analytical Study of Laser-Computed Tomography: Application to Air Pollution," Journal of the Optical Society of America, **69**, 1423 (1979).
- D. C. Wolfe, Jr., and R. L. Byer, "Model Studies of Laser Absorption Computed Tomography for Remote Air-Pollution Measurement," Applied Optics, **21**, 1165 (April 1982).

8. CATALYSIS RESEARCH

Investigator: Professor J. Collman
Department of Chemistry

Exploratory Funding: \$14K

Project Description:

An efficient electrode catalyst for the reduction of oxygen to water has long been recognized as an important goal. Such a catalyst would remove the largest single obstacle to practical fuel cells, air batteries, water electrolysis for large-scale energy storage, and water photolysis by sunlight. It would also make possible large power savings in caustic-chlorine cells by substituting oxygen reduction for hydrogen evolution. Despite much empirical work to find such a catalyst, none exists. The best known, platinum, is expensive, and the current density it can support is several orders of magnitude too low at potentials close enough to the equilibrium potential to be effective.

For the past several years, Prof. Collman and his students have been preparing some exotic molecules in which two flat porphyrin rings are held in a close, "face-to-face" geometry. Each porphyrin contains a cobalt atom. Professor Collman's hypothesis was that two such closely spaced metal ions could collectively engage oxygen and facilitate its reduction to water. A series of these compounds has been prepared and examined as electrode catalysts in Prof. Anson's laboratory at the California Institute of Technology.

When adsorbed as a monolayer on graphite electrodes, certain face-to-face porphyrin complexes as their bis-cobalt derivatives are active catalysts for the four-electron reduction of oxygen to water. At potentials as high as 0.72 V versus the normal hydrogen electrode, these promote the reduction of oxygen to water without forming free hydrogen peroxide, which is itself not reduced. Reaction rates are very high (turnover numbers $> 300 \text{ sec}^{-1}$). This four-electron reaction requires an acidic medium ($\text{pH} < 3$) and is exquisitely sensitive to the geometry of the interporphyrin cavity; only the most closely spaced, coaxially oriented dimers show this activity. Cobalt derivatives of all other porphyrin dimers and monomers catalyze only the two-electron reduction of oxygen to hydrogen peroxide, at much more negative potentials. According to recent electrochemical studies by Anson and his student, Richard Durand, the mechanism of the four-electron reduction is quite different from the two-electron reaction.

Ongoing work under Collman is directed towards improvements of these catalysts in terms of their effective potential and their durability. The mechanism of this reaction and the structural characterization of these catalysts are also being explored, so that it may be possible to invent less expensive catalysts based on this principle.

The exploratory research funding allowed Prof. Collman to obtain a stirred high-pressure autoclave, which is being used by Collman and his students in a new experimental technique for distinguishing heterogeneous or

particulate metal catalysts from truly homogeneous catalysts. This technique involves the use of ^{13}C labeled, cross-linked, polymeric substrates. Many reports in recent literature describe soluble compounds which serve as pre-catalysts to form unusual, apparently homogeneous catalysts; however, in many instances it is quite plausible that actual microscopic metal particles are the true catalysts. Collman expects to distinguish the truly homogeneous from the particulate catalysts, since the former are able to penetrate cross-linked polymers and the latter are not. He has demonstrated the first premise experimentally. These experiments required the higher pressures provided by the autoclave.

A second project in which Collman and his students have used this system is based on the observation that many homogeneously catalyzed reactions may involve a bimetallic step in the overall cyclic reaction mechanism. That is, two metal complexes may have to come together in order to consummate the reaction cycle. Since this step may not be rate determining, it has been overlooked in the past. Collman has "site isolated" otherwise homogeneous Oxo catalysts by attaching these to silicon--thus preventing the bimetallic step. This way, he turns off reactions such as hydroformation. Collman thinks it should be possible to turn an Oxo catalyst into a Fischer-Tropsch catalyst and to use this technique to invent new catalysts of the Oxo type. Many of these reactions require high pressure (especially the Fischer-Tropsch processes), which the autoclave provides.

Professor Collman's work in this area is now supported by the National Science Foundation.

Selected Publications

1. J. P. Collman et al., "Electrode Catalysis of the Four-Electron Reduction of Oxygen to Water by Dicobalt Face-to-Face Porphyrins," Journal of the American Chemical Society, **102**, 6027-6036 (1980).
2. J. P. Collman et al., "Molecular Engineering: The Design and Synthesis of Catalysts for the Rapid 4-Electron Reduction of Molecular Oxygen to Water," Organic Synthesis Today and Tomorrow (Proceedings, IUPAC meeting, June 1980, Madison, Wis.), B. M. Trost and C. R. Hutchinson, editors. Oxford, Pergamon Press, 1981, pp. 29-45.
3. M. Marrocco, III, "'Face-to-Face' Porphyrin Catalysts for the Electroreduction of Oxygen: MCD, Electrochemistry, and Electrocatalysis," Ph.D. dissertation, Stanford University, March 1980.
4. J. P. Collman, et al., "Further Studies of the Dimeric Beta-Linked 'Face-to-Face Four' Porphyrin: FTF4," Journal of the American Chemical Society, **105**, 2694-2699 (1983).
5. J. P. Collman et al., "Mixed-Metal Face-to-Face Porphyrin Dimers," Journal of the American Chemical Society, **105**, 2699-2703 (1983).
6. J. P. Collman et al., "Two New Members of the Dimeric Beta-Linked Face-to-Face Porphyrin Family: FTF4* and FTF3," Journal of the American Chemical Society, **105**, 2704-2710 (1983).

7. J. P. Collman, et al., "Mechanistic Aspects of the Catalytic Reduction of Dioxygen by Cofacial Metalloporphyrins," Journal of the American Chemical Society, **105**, 2710-2718 (1983).
8. J. P. Ollman, et al., "A Silica-Supported Rhodium Hydroformylation Catalyst: Evidence for Dinuclear Elimination," Journal of the American Chemical Society, **105**, 7288-7294 (1983).
9. J. P. Collman, et al., "Polymer-Bound Substrates: A Method to Distinguish between Homogeneous and Heterogeneous Catalysis," Journal of the American Chemical Society, in press.

9. STUDIES OF THE TRANSPORT DISENGAGEMENT REGION OF A FLUIDIZED BED

Investigator: Professor J. K. Eaton
Department of Mechanical Engineering

Exploratory Research Funding: \$10K

Project Description:

Professor Eaton is very knowledgeable in the area of separated fluid flow. He sought to apply this expertise to improve the disengagement of particles from the flow in a fluidized bed.

Disengagement occurs in the upper portion of the vessel, where the fluid-flow velocity is reduced. In flows without particles, passages of the type usually employed exhibit very large-amplitude unsteady separation, and Eaton's idea was that his knowledge of this phenomenon and how to control it could lead to improved designs for disengagement.

The exploratory research funding enabled him to construct a special, variable geometry, fluidized bed research facility and to obtain optical instrumentation for particle velocity and distribution measurement.

Measurements revealed striking differences between particle-laden and particle-free separated flow. It has led him into a new and expanding program of generic research on particle-laden flows.

Professor Eaton's work in this area has since been supported by industrial grants, principally from Union Carbide and S. Levy, Inc.

10. INTEGRATED GASIFICATION COMBINED-CYCLE SYSTEMS FOR POWER GENERATION

Investigator: Professor R. H. Eustis
Department of Mechanical Engineering

Exploratory Research Funding: \$10K

Project Description:

Professor Eustis, leader of Stanford's substantial program in MHD power research, wanted to explore some new schemes for integrated power generation with other functions, such as coal gasification. The exploratory research funding enabled him and two students to develop computer programs for this analysis.

These programs were used to investigate parameters of the combined coal gasification-gas turbine-steam cycle and helped to elucidate the need for further work. A proposal was made to and accepted by EPRI on "Off Design Operation of Integrated Coal Gasification Combined Cycle Systems."

A number of studies have been made of IGCC systems operating at a single design point in order to evaluate the general concepts. However, it is necessary to look at the operating envelope of the IGCC systems and to consider the off-design performance. The off-design operation may come about because of load fluctuation or because of component failures or degradation which may force operation at conditions which are less than optimum, but necessary in order to maintain load. In some combined systems, a large amount of the energy for steam generation is derived from the coal gasifier. Thus, if there is a problem in the gasifier, for example, there is a direct and large influence on the steam system. It is an object of the follow-on research program to study the off-design performance of IGCC plant steam systems and to predict the difficulties which might ensue for various failure modes and to suggest design procedures for minimizing such difficulties.

A related problem which concerns off-design performance has to do with the possible staged construction of IGCC plants. With natural gas pricing in its present chaotic condition, utilities are interested in using natural gas as long as its price is low, but having the option of converting to a coal-gasifier system at a later date. The question then arises, how can a system best be designed which will operate with natural gas and later permit integration of the gasifier at a minimum cost and with minimum impact on the power system? At the same time the cost and performance restrictions are considered, the possibility of optimizing efficiency must also be taken into account. A second aspect of the follow-on work, then, is to consider alternative steam system designs for the staged construction of IGCC plants.

Selected Publications

- T. D. Simons, M. Mitchner, and R. H. Eustis, "A Generalized Quasi-One-Dimensional Electrical Model for MHD Generators," 20th Symposium on Engineering Aspects of MHD, Irvine, CA, June, 1982.
- D. Roseman, T. Nakamura, and R. Eustis, "Current Distribution and Nonuniformity Experiments in a Combustion-Driven MHD Disk Generator," 20th Symposium on Engineering Aspects of MHD, Irvine, CA, June, 1982.
- T. D. Simons, R. H. Eustis, and M. Mitchner, "Measurements of Propagating Acoustic and Entropy Waves in a Combustion MHD Generator," 20th Symposium on Engineering Aspects of MHD, Irvine, CA, June, 1982.
- M. C. Wynn and R. H. Eustis, "Effects of Core Nonuniformities on the Performance of MHD Generators," 20th Symposium on Engineering Aspects of MHD, Irvine, CA, June, 1982.
- M. C. Wynn and R. H. Eustis, "Effects of Core Nonuniformities on the Performance of MHD Generators," submitted to AIAA, March 1983.
- R. P. Heydt and R. H. Eustis, "Rod Electrodes for Combustion MHD Generators," 21st Symposium on Engineering Aspects of MHD, Argonne, IL, 1983.
- M. C. Wynn and R. H. Eustis, "Effects of Core Nonuniformities on the Performance of MHD Generators," VIIIth International Conference on MHD Electrical Power Generation, Moscow, USSR, September 1983.
- K. D. Annen and R. H. Eustis, "System of an MHD/Gas Turbine Combined-Cycle Baseload Power Plant," submitted to AIAA Journal of Energy.

11. COMBUSTION RESEARCH

Investigator: Professors R. K. Hanson and C. T. Bowman
Department of Mechanical Engineering

Exploratory Research Funding: \$15K

Project Description:

Professor Hanson is an expert in optical diagnostics. This exploratory research funding, one of the first made under this institutional program, produced very substantial return. The funding enabled the purchase of a new type of tunable dye laser. The laser can be tuned finely across individual electronic transitions of the molecular species under study, and hence can be used to determine the concentration of radical species such as OH. It has been used in conjunction with a shock tube to make a number of critical measurements of kinetic parameters important in combustion reactions. This combustion diagnostics system was the first of its kind in the United States.

The acquisition of this capability acted like a magnet, attracting other support. Over a five-year period, Prof. Hanson built what is now one of the most outstanding combustion diagnostics research centers in the world. It was selected by the Air Force Office of Scientific Research, in a national competition, as the site for deployment of major funds for equipment and research in this area. Over \$500K of new equipment for combustion diagnostics has resulted from this development. About a dozen Ph.D. students are involved in this program.

Several techniques are under development, including: tunable laser fiber-optic absorption and fluorescence probes for species and temperature measurements; tunable diode laser techniques for measurements of combustion species in clean and sooting flames; quantitative flow-field visualization schemes using laser-induced fluorescence and rectangular arrays of miniature photodetectors to obtain instantaneous images of species and temperature distribution in a plane; fiberoptic links for transfer of laser light to remote monitoring locations; and modifications to a commercial dye laser system to permit rapid, high-resolution, spectral scans in high-temperature gases.

This work is now supported by the Department of Energy, the Air Force Office of Scientific Research, and private industry.

Selected Publications

- R. K. Hanson, "Absorption Spectroscopy in Sooting Flames Using a Tunable Diode Laser," Applied Optics, **19**, 482 (1980).
- R. K. Hanson et al., "Absorption Spectroscopy of Combustion Gases Using a Tunable Infrared Diode Laser," Laser Probes in Chemistry, ACS Symposium Series, **134**, 413 (1980).
- G. Kychakoff and R. K. Hanson, "Optical Fiber Probe Using Tunable Laser Absorption Spectroscopy for Combustion Measurements," Los Alamos Conference on Optics, SPIE, **288**, 236-240 (1981).
- G. Kychakoff et al., "Quantitative Visualization of Combustion Species in a Plane," Applied Optics, **21**, 3225 (1982).
- S. M. Schoenung, "Tunable Diode Laser Absorption Probe Techniques for Species Measurements in Combustion Gases," Ph.D. dissertation, Stanford University, March 1982.
- S. M. Schoenung and R. K. Hanson, "CO and Temperature Measurements in a Flat Flame by Laser Spectroscopy and Probe Techniques," Combustion Science and Technology, **24**, 237 (1981).
- S. M. Schoenung and R. K. Hanson, "Laser Absorption Sampling Probe for Temporally and Spatially Resolved Combustion Measurements," Applied Optics, **21**, 1767 (1982).
- P. L. Varghese and R. K. Hanson, "Collision Width Measurements of CO in Combustion Gases Using a Tunable Diode Laser," Journal of Quantitative Spectroscopy and Radiative Transfer, **26**, 339-347 (1981).
- B. Hiller J. C. McDaniel, E. C. Rea, Jr., and R. K. Hanson, "Laser-Induced Fluorescence Technique for Velocity Field Measurements in Subsonic Gas Flows," Optics Letters, **8**, 474 (1983).
- R. K. Hanson, S. Salimian, G. Kychakoff, and R. A. Booman, "Shock-Tube Absorption Measurements of OH Using Remotely Located Dye Laser," Applied Optics, **21**, 641 (1983).

12. FEASIBILITY STUDIES FOR A COAL-CONSUMING FUEL CELL

Investigator: Professor R. A. Huggins
Department of Materials Science and Engineering

Exploratory Research Funding: \$65K

Project Description:

This project was initiated to investigate the feasibility of a new approach to an old goal, the direct electrochemical conversion of coal to electrical energy. Because such a process is not limited by the Carnot Cycle constraints, it is theoretically possible to achieve significantly greater efficiencies than can be obtained by the utilization of gasification, liquefaction, or chemical combustion, combined with the use of a heat engine.

This new approach has several features which make it quite different from previous attempts to achieve this goal. It involves the utilization of an oxide ion-conducting solid electrolyte, whereas all previous approaches have employed liquid electrolytes. This possibility, which resulted from recent progress in solid-state electrochemistry (the applicational aspects of which are coming to be called "solid state ionics"), has some very important potential advantages. One of these is that one can now consider the possibility of utilizing liquid electrodes, or liquid-solid mixtures.

The second major deviation from conventional approaches to electrochemical cells--the utilization of a mixed (ionic and electronic) conducting liquid matrix to contain the coal particles, which are consumed by reaction with the oxygen (from air), which is transported across the cell. This procedure provides a very important kinetic advantage, for the reaction can then take place over the complete surface of each small coal particle, an extremely large surface area, rather than being limited by the surface area of the electrolyte. By being both an oxygen conductor and an electronic conductor, the liquid matrix material can also serve as the electronic current collector for the cell.

Such a cell would operate by transport of oxygen from air through the solid electrolyte (thus producing a voltage) into the two-phase coal-mixed-conductor electrode, where it reacts with the coal to form CO or CO₂, depending upon the temperature, as well as water and other by-products. These products leave the cell as a recoverable gas. Inert impurities in the coal, such as aluminum oxide and silicon dioxide, will separate by either sinking to the bottom or floating to the top of the liquid. The presence of the coal on the negative side of the cell provides a low oxygen activity on that side of the solid electrolyte. The difference between this low oxygen activity and the oxygen activity on the other side of the cell--determined by the presence of air or oxygen--provides a cell voltage of the order of one volt, depending upon the temperature, the coal composition, and kinetic features of the system.

Work on this program involves three major issues:

1. demonstration of the general feasibility of this concept,
2. the selection (or discovery) of a suitable oxide ion-conducting electrolyte, and
3. the selection (or discovery) of a suitable mixed-conducting material to use in the coal-containing electrode compartment.

One of the critical features is the solid electrolyte. This material must have a high value of ionic conductivity and a low electronic conductivity. It must be both mechanically and chemically stable at the temperature of operation, and over the range of thermodynamic parameters (e.g., oxygen activity) imposed by the air on one side and the coal-liquid matrix on the other.

For somewhat over a decade, it has been known that several oxides can act as good, solid electrolytes for oxide ions. The best known of these materials is stabilized zirconia, which is presently being introduced as an oxygen sensor in automobile exhaust systems in order to optimize the mixture going into the combustion process. A few other oxides, such as thorium and ceria, have also been used for related purposes, either to measure or to control the oxygen activity or concentration in gases, liquids, or solids.

The second critical material in a coal-consuming fuel cell is the oxygen-transporting mixed conductor that operates as the liquid matrix for the coal electrode. This material must transport oxygen rapidly from the solid electrolyte to the surfaces of the coal particles, where the liquid in the thermodynamic environment imposed by the coal (e.g., an oxygen activity of about 10^{-23} atmospheres at 800°C). In addition, it must wet both the solid electrolyte and the surfaces of the fine coal particles in order to provide the desired high-contact area. It must also not contain species which will react with oxygen at a lower oxygen activity than that produced by the coal, and must not react chemically with either the coal or the solid electrolyte. In addition, it must be inexpensive, non-toxic, and non-corrosive.

Experiments conducted under the exploratory research funding showed that a solid electrolyte-based fuel cell of this type can produce the voltages expected from known thermodynamic data on the carbon/oxygen reaction at elevated temperatures. Initial experiments were performed utilizing a zirconia tube as the solid electrolyte, with air in contact with a thin film of porous platinum as the positive electrode. Both samples of coal and a finely divided non-crystalline carbon have been used in the other side of such cells. In all cases, the theoretical voltage is obtained, but only at quite low currents, as expected.

Oxygen-transporting molten metals were the first liquid matrix materials investigated as constituents of the coal-liquid slurry. Cells containing them also gave proper voltages, but had rather slow kinetics. This discovery was what one should expect from the limited solubility of oxygen in such materials. These experiments, however, did confirm the validity of the general concept.

The exploratory work also looked at the use of other liquids that should be more suitable for this purpose, including investigations in several molten salt systems that readily dissolve oxygen, in which one should be able to introduce electronic conductionably appropriate doping.

It has thus been shown that this novel concept has general merit, and the critical requirements and necessary properties of the important components of the system are now clear. In order to move toward a practical embodiment, the major effort is now directed toward finding suitable materials to perform the necessary functions. The most unusual requirements and the area in which one can obtain the least guidance from prior work have to do with the liquid material in contact with the finely dispersed coal in the negative electrode compartment. The combination of required properties is quite unusual, and there is almost no directly applicable basic information available in the literature. However, the understanding gained of the thermodynamic relationships in ternary and quaternary oxide systems in connection with a recent Ph.D. dissertation should provide substantial guidance in the selection and interpretation of critical experiments to evaluate the important parameters of the materials required for this type of new application.

The approaches that appear to provide the best approach appear to be based upon the solution of oxide ions in other electronically conducting liquid solvents, and the doping of stable low-melting salt and oxyanion liquids to increase their electronic conductivity. Work in such areas is highly exploratory, and it is not possible either to plan in detail or to predict with any degree of precision exactly how investigations of this type will turn out. It is fair to say, however, that no fundamentally limiting features of this approach have been found and that it is reasonable to assume that satisfactory solutions will be found.

The progress of this program was dealt a severe blow when Dr. Werner Weppner, who has been brought to Stanford by Professor Huggins to work on this program, decided to return to Germany. Professor Huggins' interest in this area continues. His work, sponsored by the Lawrence-Berkeley Laboratory and the Sandia National Laboratory, has been strongly influenced by the findings made under this exploratory research program.

13. PULVERIZED COAL COMBUSTION

Investigator: Professor C. H. Kruger
Department of Mechanical Engineering

Exploratory Research Funding: \$55K

Project Description:

This program is part of the extensive combustion research program in the Department of Mechanical Engineering, which involves four faculty members and about a dozen Ph.D. students. A flow-tube reactor is used to study the reactivity of pulverized coals under uniform and controlled conditions. The reactor system incorporates optical diagnostics as well as probe-sampling techniques to measure the reactivity of coals with differing physical and chemical properties. Results of the measurements can aid in the understanding of the mechanism of coal reaction and combustion and provide useful data for the design and development of coal-combustion systems.

Using the exploratory research funding, the flow-tube reactor and associated diagnostics were fabricated, and the experimental conditions were well characterized. Oxidation reactivity measurements have been made with Montana Rosebud, Illinois No. 6, and Utah coals. The results show interesting and unexpected dependences of the rate of combustion on gas temperature and oxygen concentration, indicating energy feedback from burning volatiles to the coal particles.

Given the complexity of pulverized coal combustion, the investigator decided to minimize the number of variables changing during the process. Ideally, only the coal properties would change during combustion, and all individual coal particles would behave quite similarly. These conditions are closely approximated by the Stanford Flow Tube Reactor.

Dilute quantities of coal are injected into a nearly isothermal flow. The coal has a negligible enthalpy addition to the gas flow and makes only small changes in the reactant gas concentration. In addition, the coal number density is low enough that complex particle-particle interactions may be ignored. Coal burnout rates are highly dependent on particle size, particle structure, and composition. At Stanford, narrowly sized pulverized coal samples reduce the variability of reaction rates between individual particles of a given type in a given flow. Thus, one obtains similarly burning coal particles emersed in a nearly isothermal and nearly constant gas-composition environment.

Optical measurements can be made at three locations for a given reactor configuration, namely, through two 4 cm diameter access ports and in the free jet of the reactor exit. The possible combinations of coal injector height, flow velocity, reactor diameter, and length provide the capability of measuring the extent of reactions at times ranging from 10 to 300 msec.

At the exit of the flow-tube reactor, an exhaust section is provided for water cooling of the hog gas effluent. Also located in this section is a

traversing sampling probe used for acquiring gas and particulate samples. The sampling probe can be positioned axially, radially, and in the azimuthal direction with the flow tube, thereby obtaining gas (CO_2 , CO , O_2) and particle data anywhere within the reactor.

The exploratory research funding enabled the apparatus to be completed and its potential demonstrated. It is now in use on a continuing pulverized-coal combustion-research program sponsored by the Department of Energy.

Selected Publications

- D. J. Holve, "An In-Situ Optical Particle-Sizing Technique," J. Energy, 4, 176-183 (1980).
- I. Leslie, M. Jost, and C. H. Kruger, "Oxidation Reactivity of Pulverized Montana Rosebud Coal During Combustion," Western States Section, Combustion Institute, April 1982. Paper 82-2.
- M. Jost, I. Leslie, and C. H. Kruger, "Oxidation Reactivity of Pulverized Montana Rosebud and Illinois No. 6 Coal During Combustion," presented at the American Institute of Chemical Engineers Summer National Meeting/Section 14 on Basic Research in Coal Combustion, Cleveland, OH, August, 1982.
- M. Jost, I. Leslie, and C. H. Kruger, "Devolatilization and Char Burnout of Pulverized Coal in an Oxidizing Environment," submitted to 20th International Symposium on Combustion, 1984.

14. CARBON DIOXIDE IMPACT

Investigator: J. A. Laurmann
Senior Research Associate
Division of Applied Mechanics

Exploratory Research Funding: \$10K

Project Description:

At a time of intense interest in the CO₂ problem, Dr. Laurmann, an atmospheric scientist, organized a team of faculty and students to gain background on the problem.

Two students worked on the project. One student developed a fossil-fuel burning rights formulation that addresses the problem of international implementation of a hypothetical decision to limit atmospheric CO₂ levels from this point of view. Another completed a review of future discounting as related to the CO₂ problem and subsequently worked on formulation for CO₂ remediation.

It had been expected that this work would develop into an important interdisciplinary team-research project on a problem of great national interest. When that interest waned, the project ended, and Dr. Laurmann left Stanford.

15. CATALYSIS RESEARCH

Investigator: Professor R. J. Madix
Department of Chemical Engineering

Exploratory Research Funding: \$15K

Project Description:

Professor Madix leads an active research group in catalysis. These funds were used to enable him to rebuild and repair a mass spectrometer, and to obtain electron diffraction apparatus and associated electronics for use in his research program, which is outlined below.

In his program, he and his students study the surface physics and chemistry of metals with a variety of analytic tools. Electronic states and chemical reactivity are extremely sensitive to changes in surface composition, even in monolayer quantities. Consequently, the effects of surface additives such as carbon, sulfur, oxygen, etc., on surface reactivity are studied. Work on metal carbides has contributed to the development of surface area molybdenum carbide catalysts which show promising catalytic activity.

The fundamental nature of the energy barrier to adsorption of molecules important in steam reforming, methanation, and ammonia synthesis is also being studied. In addition, the effect of surface impurities on the rates of fast reactions at metal surfaces is studied.

His energy-related catalysis research is now supported by the Department of Energy and the National Science Foundation.

Selected Publications

- Barteau, M. A., and R. J. Madix, "A Study of the Relative Bronstead Acidities of Surface Complexes on AG(110)," Surface Sci., 120, 262 (1982).
- Gdowski, G., and R. J. Madix, "The Kinetics and Mechanism of the Hydrogen Oxygen Reaction on Pt(s)-(9(111)x(100))," Surface Sci., 119, 184 (1982).
- Barteau, M. A., and R. J. Madix, "Photoelectron Spectra of Adsorbed Carbonates," J. Electron Spect., 31, 101 (1983).
- Abbas, N., and R. J. Madix, "The Effect of Structured Overlayers of Sulfur on the Decomposition of Formic Acid on PT(111)," Appl. Surface Sci., in press.
- Madix, R. J., S. B. Lee, and M. Thornburg, "The Effects of Adsorbed Sulfur on the Adsorption and Reaction of CO and Methanol on NI(100)," J. Vac. Sci. Tech. A, 1254 (1983).
- Madix, R. J., J. L. Gland, G. E. Mitchell, and B. A. Sexton, "Identification of the Intermediates in the Dehydration of Formic Acid on Ni(110) by High-Resolution Electron-Energy-Loss Vibrational Spectroscopy," Surface Sci., 125, 481 (1983).
- Outka, D. A., C. M. Friend, S. Jorgensen, and R. J. Madix, "Adsorption and Hydrogenation of Acetylene on Cu(110) and Cu(110)-O Surfaces," J. Am. Chem. Soc., 105, 3468 (1983).
- Madix, R. J., "Combined Vibrational/Temperature Programmed-Reaction Spectroscopy Studies of Reaction Intermediates on Metal Surfaces," J. Electron. Spec. and Rel. Phen., 29, 25 (1983)

16. MICROBIAL DESULFURIZATION OF COAL

Investigator: Professor A. Matin
Department of Medical Microbiology

Exploratory Research Funding: \$15K

Project Description

This was perhaps the highest-risk, high-payoff exploratory research project funded under this program. The idea was to explore the use of microbiology to desulfurize fuels such as coal.

Although started near the end of the institutional grant program, this effort produced some promising results. Studies with naturally existing organisms that are capable of removing sulfur from fuels gave encouraging results, and it seems certain that genetic manipulation of these bacteria, with respect to their acid tolerance and sulfur-oxidation potential, will make this process economically very attractive.

Matin has made very good progress in elucidating the physiology of acidophilism in these bacteria; this property is very relevant in desulfurization. Considerable progress has also been made in genetic studies. Thus, he has succeeded in identifying several plasmids in these bacteria, and a line of experimentation nearing completion promises to identify the function of some of these plasmids. In addition, he has succeeded in isolating pure-culture, two-bacterial species that are capable of degrading dibenzylthiophene.

Selected Publications

1. Zychlinsky, E., and A. Matin, "Cytoplasmic pH Homeostasis in an Acidophilic Bacterium (Thiobacillus Acidophilus), J. Bacteriology, **156**, 1352-1355 (1983).
2. Zychlinsky, E., and A. Matin, "Effect of Starvation on the Cytoplasmic pH and the Protonmotive Force of an Acidophilic Bacterium (Thiobacillus Acidophilus), J. Bacteriol., **153**, 371-374 (1983).
3. Matin, A., and M. K. Matin, "The Protonmotive Force and the pH in Spheroplasts of Thiobacillus Acidophilus, J. Gen. Microbiol., **1328**, 3071-3075 (1982).
4. Matin, A., B. Wilson, E. Zychlinsky, and M. K. Matin, "Proton Motive Force and the Physiological Basis of Delta pH Maintenance in Thiobacillus Acidophilus, J. Bacteriol., **150**, 582-591 (1982).

17. COAL DIAGNOSTICS BY ACOUSTIC MICROSCOPY

Investigator: Professor C. Quate
Department of Applied Physics

Exploratory Research Funding: \$40K

Project Description:

The objective of this exploratory study was to establish the feasibility of using acoustic waves to monitor both the elastic properties and optical absorption of vitrinite--an important maceral of coal. Professor Quate is an expert in acoustics and the pioneer developer of acoustic microscopy.

Optical reflectance is an established technique for measuring the rank of coal. It is effective and widely used for high-rank coal such as that used in the coking industry. However, it is of limited use for the lower-rank coals, which have become important as a prime source of energy. The idea was to establish that acoustic reflection from vitrinite could be used to characterize the carbon content of a broad range of coals. Quate also proposed that the techniques used in photoacoustics could be used to monitor the optical absorption of vitrinite, efficiently and quickly.

With photoacoustics, it is possible to measure the optical absorption by monitoring the acoustic waves emitted from the region where the optical energy is being absorbed. In that system, the optical beam is modulated with a frequency, f_m . The optical beam heats the sample; in turn, the sample expands and contracts with a periodicity equal to the modulation frequency. The periodic expansion generates a sound wave at f_m . It is this wave that we detect within the acoustic system.

The optical absorption of vitrinite is high when compared to the optical reflectance, which is near 1%. A practical method for monitoring optical absorption should be superior. But in what way? As mentioned above, optical reflectance is limited to a narrow range of coals--namely, those of high rank. Coals of low rank, which constitute the majority of U.S. deposits and shale, are difficult to characterize in this way. Improved techniques for characterizing the entire range of coals are needed. Quate believes that acoustic reflection and optical absorption through photoacoustics could provide this new methodology.

The exploratory research funding made it possible for Quate and his students to follow several avenues and establish guidelines. These can be summarized:

1. Working relationships with laboratories engaged in research in this field of coal characterization were established.
2. Samples with known properties were acquired from these laboratories and limited measurements of the acoustic reflectance from these samples were made.
3. An argon laser was incorporated in an instrument for photoacoustic imaging. Professor Quate participated in the Conference of Coal

Characterization in West Virginia with an invited paper of acoustic microscopy.

4. Photoacoustic images were successfully recorded. These images are recorded in 15 seconds with a high signal-to-noise ratio. This compares to previous recording which required 15 minutes or more for recording.
5. Photoacoustic images of coal samples were made with samples provided by the Chevron Research Laboratory.
6. Commercial instruments are now under construction by Leitz-Wetzlar in West Germany. Leitz has been a pioneer in the fabrication of optical microscopes for coal characterization. It is expected that they will be at the forefront with instrumentation that will enable us to characterize coal with acoustic reflectance. Acoustic microscopes will also be produced by Olympus and Hitachi in Japan and VG in England.

In summary, the exploratory research funding allowed Quate and his students to adapt his acoustic microscope in a way that allows us to present the reflectance information--not in the form of images, but in the form of histograms. This has made it possible to measure the acoustic reflectance of vitrinite from two different coal samples. In each case, the reflectance was about 30 times higher than the optical reflectance from the samples. This leads one to suggest that acoustic reflectance measurements will allow characterization of a wide range of coal and shales.

The continuing work of Professor Quate and his students in acoustic microscopy is supported by the Office of Naval Research, the Air Force Office of Scientific Research, and the National Science Foundation.

Selected Publications

- H. K. Wickramasinghe, R. C. Bray, V. Jipson, C. F. Quate, and J. R. Salcedo, "Photoacoustics on a Microscopic Scale," Appl. Phys. Lett., **33**, 923-925, (21 December, 1978).
- C. F. Quate, A. Atalar, and H. K. Wickramasinghe, "Acoustic Microscopy with Mechanical Scanning--A Review," Proc. IEEE, **67**, 1092-1114 (August 1979).
- C. F. Quate, "Acoustic Microscopy," Scientific American, **241**, 58-66 (October, 1979).
- R. C. Bray, J. Calhoun, R. Koch, and C. F. Quate, "Film Adhesion Studies with the Acoustic Microscope," J. Thin Solid Films, **74**, 295-302 (1980).
- C. F. Quate, "Acoustic Microscopy for the Characterization of Coal," AIP Conference Proceedings, No. 70, Chemistry and Physics of Coal Utilization--1980, B. R. Cooper and L. Petrakis, eds. (American Institute of Physics, New York, 1981), 141-153.
- R. C. Bray, "Acoustic and Photoacoustic Microscopy," Ph.D. thesis, Stanford University (March 1981).

18. FLUID MECHANICS IN INTERNAL COMBUSTION ENGINES

Investigator: Professor W. C. Reynolds
Department of Mechanical Engineering

Exploratory Funding: \$15K

Project Description:

The objectives of this work are to understand how the fluid mechanical processes occurring within internal combustion engine cylinders control the combustion and mixing processes that are important to efficient engine operation and low pollutant formation.

The research is being conducted in a unique flow-diagnostic engine. The engine has a transparent cylinder and piston, computer-controlled valves with a fully electronic cam shaft, and many other novel features appropriate to the research objective. The current work deals with the fluid mechanics of the mixing process of the incoming charge with residual gas left after the previous combustion cycle. Many other interesting fluid mechanical problems can be studied in this engine, and a broad range of research is planned for the future.

The development of the flow diagnostic engine was initiated in 1979. The most significant major accomplishment to date has been the development of a new holographically corrected schlieren system that enables visualization of the flow within the cylinder without optical distortion caused by the cylinder curvature.

The exploratory research funding assisted in the development of this unique research facility. Ongoing research in the diagnostics engine is now supported by the General Motors Corporation.

Selected Publications

W. C. Reynolds, "Modeling of Fluid Motion of Engines--An Introductory Overview," Combustion Modeling and Reciprocating Engines, New York and London: Plenum Press, 1980.

R. M. Richman and W. C. Reynolds, "The Flow Diagnostics Engine: A New System for Piston Engine Research," Tech. Report FDE-1, Thermosciences Division, Department of Mechanical Engineering, Stanford University, 1982.

See also SAE Paper 840379)

19. POLYMER HYDROMECHANICS

Investigator: Professor G. Fuller
Department of Chemical Engineering

Exploratory Research Funding: \$10K

Project Description:

Professor Fuller engages in research into a broad range of topics involving the fluid dynamics of polymeric and colloidal liquids. In this work, he is studying the response of adsorbed polymer chains to hydrodynamic forces. This research is of fundamental importance to the process of polymer flooding developed for use in enhanced oil recovery. In that process, small quantities of polymer additives are used in the pusher fluid (water) in oil-reservoir flooding operations in order to enhance the stability of the water/oil interface. The subsequent adsorption of the polymer from the solution onto the surrounding porous media is an important consideration, due to the irreversible loss of polymer and the associated changes in the hydrodynamic resistance of the porous media due to clogging of the small pores of the oil-bearing rock. This project is investigating the consequences of hydrodynamic forces on the process of polymer adsorption by experimentally determining the structure of adsorbed polymer layers during flow processes.

These measurements are performed using a Fourier transform ellipsometer which was constructed using the exploratory research funding supplied by the Energy Institute. This device has made it possible, for the first time, to determine the thickness and surface concentration of adsorbed polymer layers directly during a flow process. Over the past three years, this research has uncovered a number of phenomena which are of critical importance to the design and operation of polymer flooding operations. It has been determined that hydrodynamic forces can have a profound influence on the kinetics of polymer adsorption and the final conformation of the adsorbed films. Significant flow-enhanced desorption of polymer chains already attached to solid surfaces was observed under operating conditions which would be typical of polymer flooding operations. Indeed, in many instances it was found that adsorbed polymer films could be entirely stripped away if the imposed hydrodynamic forces were large enough. Similarly, the kinetics of the adsorption process itself was found to be a strong function of the flow conditions. Here, moderate hydrodynamic forces were observed to dramatically reduce the rate of adsorption and the final surface concentration.

The results indicated above clearly demonstrate the importance of considering the consequences of hydrodynamic forces in processes such as polymer flooding where polymer adsorption occurs in the presence of a flow.

The results which were obtained using the experimental apparatus constructed with funding from the Energy Institute has made it possible to attract long-term support from the Chemical Process Engineering Division of the National Science Foundation.

Selected Publications

1. G. G. Fuller, Dynamics of Adsorbed Polymer Chains Subjected to Flow: The Dumbbell Model," J. Polym. Sci.: Polym. Phys. Ed., **21**, 151 (1983).
2. G. G. Fuller and J.-J. Lee, "Ellipsometry Studies of Adsorbed Polymer Chains Subjected to Flow," Macromolecules, 1984, in press.
3. G. G. Fuller and J.-J. Lee, "Flow-Enhanced Desorption of Adsorbed Polymer Chains," accepted by ACS Symposium series, 1983.
4. G. G. Fuller and J.-J. Lee, "The Kinetics of Polymer Adsorption in the Presence of Flow," manuscript in preparation.

20. HIGH-TEMPERATURE DEFORMATION

Investigator: Professor A. K. Miller
Department of Materials Science and Engineering

Exploratory Research Funding: \$10K

Project Description:

The investigator and his students are developing models which can predict fracture of metals and alloys. Particular emphasis is placed on materials-limited aspects of energy technology, which, in turn, leads to an emphasis on predicting fracture of high-temperature structural materials and fracture under complex histories and environments. It is anticipated that the models developed could be used either directly by high-temperature structural design analysts for life prediction of specific components or indirectly to guide the development of design rules, codes, and so on. This is the principal area of research by Professor Miller and his students.

It is advantageous to try to represent the fundamental physical processes by which small "elements" of material fail under cyclic loading and then to numerically integrate these more fundamental local failure events into quantitative predictions of crack initiation, short crack growth, and long crack propagation. This kind of physically based, numerically integrated model for fatigue can automatically predict failure under complex histories (cumulative damage) and eventually under multiaxial loadings.

Since fracture in metals and alloys is generally the result of nonelastic deformation, development of improved constitutive equations has been and still is a major activity within this project.

Development of a fairly broad, general, and physically based model for deformation and fracture encompasses a large number of aspects, many of them closely interrelated. The project was divided into separate tasks. Past work was on solute strengthening, back stresses, subgrain strengthening, and forest dislocation hardening, with emphasis on modeling these using the "MATMOD" constitutive equations. Current work is on modeling of strain softening. "MATMOD-4V" equations have been developed for this work in which specific representations are made of the roles of both short-range and long-range back stresses, of forest dislocations, and of cellular substructures. With these equations, strain softening under a variety of conditions can be predicted. In cooperation with researchers at the Los Alamos Scientific Laboratory, work is also under way on modeling of multiaxial plastic flow with the "MATMOD" approach.

A major current task is the development of a unified model for fatigue crack initiation and growth. This model, which addresses many aspects of fatigue failure, including the small-flaw problem, represents significant progress towards a "general" model for prediction of damage accumulation and failure in cyclically loaded structures. The unified fatigue model is being designed to mesh smoothly with the "MATMOD" constitutive equations to predict elevated-temperature fatigue resistance, including creep-fatigue interactions,

and with the "SCCIG" model for stress-corrosion crack initiation and growth, thus predicting environmental effects on fatigue (corrosion fatigue).

With support from the exploratory research program and other sources, the obsolete control unit of an MTS servo-controlled mechanical testing system was replaced by an up-to-date electronic control console. With this upgraded system and a reversed torsion attachment designed and fabricated at Stanford, complex cyclic torsion tests up to $\pm 20\%$ strain amplitude can be performed.

The investigator has shown that the back stress ratio as measured by the Bauschinger effect is constant with increasing stress, but that this ratio is different from the back stress ratio as measured by a stress-transient experiment. Other important results were obtained.

Presence of the new electronics for the MTS system has allowed the investigator and his students to add a "Wavetek" arbitrary waveform generator, which allows interrupted cyclic tests and other experiments beyond the MTS system's standard capabilities.

In summary, the equipment has been an invaluable aid in the investigator's development of improved constitutive equations for predicting non-elastic deformation under complex histories.

Professor Miller's work in this area is now supported by the Department of Energy (Office of Basic Energy Sciences) and the Electric Power Research Institute (Nuclear Power Division).

Selected Publications

- K. D. Challenger and A. K. Miller, "Elevated-temperature Fatigue with Hold time in a Low Alloy Steel: A Predictive Correlation," Journal of Materials for Energy Systems, 3, 51-61 (1981).
- K. D. Challenger, A. K. Miller, and C. R. Brinkman, "An Explanation for the Effects of Hold Periods on the Elevated Temperature Fatigue Behavior of 2 1/4 Cr-1Mo Steel," Journal of Engineering Materials and Technology, 103, 7-14 (1981).
- K. S. Chan and A. K. Miller, "Prediction of Fatigue Failure in Structural Alloys: Initiation and Crack Propagation," 8th International Symposium for Testing and Failure Analysis, San Jose, CA., October 26, 1982.
- K. S. Chan and A. K. Miller, "FATIGMOD: A Unified Phenomenological Model for Predicting Fatigue Crack Initiation and Propagation," ASME Conference on Advances in Life-Prediction Methods, Albany, NY, April 18-20, 1983.
- M. E. Kassner, "The Separate Roles of Forest Dislocations and Subgrains in the Isotropic Hardening of Type 304 Stainless Steel," Ph.D. dissertation, Stanford University, March 1981.
- M. E. Kassner, "Alterations in the Microstructure of 304 Stainless Steel Produced by Small Strain Deformation at Ambient Temperature," manuscript, 1982.

- M. E. Kassner, A. K. Miller, and O. D. Sherby, "The Separate Roles of Subgrains and Forest Dislocations in the Isotropic Hardening of Type 304 Stainless Steel," Metallurgical Transactions, 1982, in press.
- M. E. Kassner, K. Rubin, and A. K. Miller, "Verification of a Microstructurally Based Equation for Elevated-Temperature Isotropic Hardening," 6th International Conference on Strength of Metals and Alloys, Melbourne, Aug. 1982, pp. 581-587.
- T. C. Lowe, "New Concepts in Modeling Strain Softening," Ph.D. dissertation, Stanford University, 1982.
- A. K. Miller, "Annual Progress Report: Modeling of Deformation and Fracture in High-Temperature Structural Materials," Dept. of Materials Science and Engineering, Stanford University, Feb. 1978, 1979, 1980, 1981, 1982.
- A. K. Miller and A. A. Ziaai-Moayyed, "Some Critical Experimental Tests of the MATMOD Equations with Respect to Directional Hardening and Cyclic Deformation," ASTM Symposium on Mechanical Testing for Deformation Model Development, Bal Harbour, Fla., Nov. 1980. American Society for Testing and Materials special technical report, ASTM STP-765, 1982, pp. 202-222.
- O. A. Ruano, A. K. Miller, and O. D. Sherby, "The Influence of Pipe Diffusion on Creep of Fine-Grain Materials," Materials Science and Engineering, 51, 9-16 (1981).
- C. G. Schmidt and A. K. Miller, "A Unified Phenomenological Model for Non-elastic Deformation of Type 3165 Stainless Steel, Part I: Derivation of the Model," Res Mechanica, 3, 109-129 (1981).
- C. G. Schmidt and A. K. Miller, "A Unified Phenomenological Model for Non-Elastic Deformation of Type 316 Stainless Steel, Part II: Fitting and Predictive Capabilities," Res Mechanica, 3, 175-193 (1981).
- C. G. Schmidt and A. K. Miller, "Modularized Program for Integrating Constitutive Equations Describing Plastic Flow Using Simple Boundary Conditions," Res Mechanica Letters, 1, 335-341 (1981).
- C. G. Schmidt and A. K. Miller, "The Effect of Solute on the Strength and Strain Hardening Behavior of Alloys: Observations and a Phenomenological Model," Acta Metallurgica, 30, 1982, 615-625 (1982).
- C. G. Schmidt et al., "The Simulation of Activation Energy Peaks in Solute-Strengthened Materials," Res Mechanica, submitted 1982.
- O. D. Sherby, A. K. Miller, and M. E. Kassner, "Subgrain Strengthening Revisited," Metals Forum, 4, 53-56 (1981).

21. DAMAGE MECHANICS

Investigator: Professor H. Herrmann
Department of Mechanical Engineering

Exploratory Research Funding: \$20K

Project Description:

The definition of damage mechanics which appears to be acceptable to most people is based on the observation that, under load, the material can exhibit newly created surfaces (e.g., small voids, small cracks), etc. which reduce its carrying capacity. This reduction is termed damage. In dimensionless form, the damage parameter can vary between zero (perfect material) and one (completely damaged material with no carrying capacity at all).

Thus the effects of damage can be measured by measuring the area or volume of cracks or voids as a function of relevant load parameters. These damage effects, which include density changes, electric resistivity changes, and many others, may be plotted against a parameter which changes them, such as time (in creep), stress, strain, or number of cycles (in fatigue). In each case, the damage curve will look qualitatively the same.

Most of the current work on damage is based on the concept introduced by L. M. Kachanov in Leningrad in 1958. The concept is based on uni-axial extension of a bar with original cross-sectional area S . As a result of applied loads, voids and cracks may be formed, such that the effective area $\tilde{S}$ across which a load can be transmitted is smaller than S . The damage D is defined as

$$D = \frac{S - \tilde{S}}{S}$$

and the effective stress $\tilde{\sigma}$

$$\tilde{\sigma} = \frac{\sigma}{1 - D}$$

Kachanov's concept can be generalized to three dimensions. The effective stress tensor can then be written as

$$\tilde{\phi} = [1 - D]^{-1} \phi$$

where the quantity in brackets is a tensor of 4th rank.

In 1981, Herrmann and his colleague, Alicia G. Herrmann, had a completely different idea how to mathematically model damage. To make sure that their idea was really original, they participated in the EUROMECH Colloquium 147 on Damage Mechanics held in Cachan (a suburb of Paris), France, in the fall of 1981. This colloquium brought together the most eminent workers in damage mechanics and permitted them to reach the conclusion that their novel idea was, indeed, original.

By contrast to the Kachanov modeling, the Herrmanns' idea is based on the fact that the creation of a void (or any other defect) changes the connectivity of the material and makes the so-called material momentum tensor not divergence-free. (For a discussion of the material momentum, or energy momentum, tensor, see the enclosed reprints.) It is their intention to explore these properties and construct an entirely different mathematical model of damage.

Extensive preparatory and exploratory studies, however, will be needed to ascertain the desirability and potential superiority of the embryonic idea.

Professor Herrmann's work in this field is now supported by the Department of Energy.

22. ENERGY MODELING

Investigators: Professors Alan Manne and James Sweeney
Departments of Operations Research and of Engineering-
Economic Systems

Exploratory Research Funding: \$10K

Project Description:

Stanford's now extensive role in energy modeling was built up largely as a result of the impetus provided by the Institute for Energy Studies. A small exploratory research grant to Profs. Alan Manne and James Sweeney helped get this program under way. Specifically, it enabled Prof. Manne to implement his ETA-Macro model at Stanford.

The enrgy modeling work at Stanford now centers around the Energy Modeling Forum, directed by Prof. Sweeney, who is the current Chairman of the Institute for Energy Studies. Founded in 1976, the Energy Modeling Forum (EMF) is affilated with the Institute for Energy Studies and administered in the Departments of Engineering-Economic Systems and Operations Research.

The EMF conducts model-comparison studies through a series of ad hoc working groups, each concentrating on a single energy topic. The working groups are composed of national and international energy modeling and energy policy and planning experts. Research assistants are among the EMF staff members of the Forum studies, and faculty members from six Stanford departments also have been actively involved.

Each working group identifies existing models relevant to the study's focus and designs a series of scenarios to illuminate the models' basic structures and behaviors and to apply these models to key informational questions. A comparison of results identifies the models' strengths and weaknesses in the context of the study topic. Simultaneously, the issue focus of the study assures that the energy policy and analysis implications of the models--the key insights--are developed and discussed. When a consensus is reached, the findings are published in reports and distributed widely to policy-makers, corporate leaders, modelers, and model users.

Seven EMF studies have been initiated to date: (1) Energy and the Economy, (2) Coal in Transition, (3) Electric Load Forecasting, (4) Aggregate Elasticity of Energy Demand, (5) U.S. Oil and Gas Supply, (6) World Oil, and (7) Macroeconomic Impacts of Energy Shocks. Each study has broadened the understanding of the nature of the relevant policy issues and the models that have, are, or could be used to address them.

The Stanford University International Energy Project (IEP) was established in April, 1979. The IEP is intended to broaden the scope of the international analysis activities conducted within the US Department of Energy and the Energy Information Administration, and to relate these to ongoing work within the academic community. The project was originally directed by prof. Henry Rowen and currently by Alan Manne.

Current work includes: (a) the analysis of natural gas trade in North America; (b) a geographically disaggregated model of international oil trade--including crude production, transportation, and refining activities; (c) a three-region intertemporal equilibrium model of energy, international trade, balance-of-payment constraints and capital flows; and (d) the International Energy Workshop (IEW).

The research of Professors Sweeney and Manne and their students in energy modeling and the EMF is now supported by the Department of Energy, the Electric Power Research Institute, the Gas Research Institute, and by a number of producing or consuming energy companies.

Selected Publications

Energy Modeling Forum, Energy and the Economy, 1 and 2, Sept. 1977. EMF Report 1.

Energy Modeling Forum, Coal in Transition: 1980-2000, 1, July 1978; 2 and 3, Sept. 1978. EMF Report 2.

Energy Modeling Forum, Electric Load Forecasting: Probing the Issues with Models, 1, April 1979; 2, March 1980. EMF Report 3.

Energy Modeling Forum, Aggregate Elasticity of Energy Demand, 1, Aug. 1980; 2, Nov. 1981. EMF Report 4.

Energy Modeling Forum, World Oil, Summary Report, Feb. 1982. EMF Report 6.

Energy Modeling Forum, "UIs. Oil and Gas Supply: EMF 5 Summary Report," working paper, April 1982, draft 6. EMF 5.4.

B. G. Hickman and H. G. Huntington, "EMF 7 Study Design," working paper, Sept. 1982. EMF 7.1, revised.

J. L. Sweeney, "The Impact of the President's Proposed Gasoline Tax and Gas-Guzzler Tax on Gasoline Consumption," DRI Energy Bulletin, Aug. 1977, pp. 6-11.

J. L. Sweeney, "The Demand for Gasoline: A Vintage Capital Model," Select Papers from Workshops on World Energy Supply and Demand, International Energy Agency, Paris, 1978, pp. 240-277.

J. L. Sweeney, "Structural/Econometric Modeling of Gasoline Consumption," Proceedings: 2nd Lawrence Symposium on Systems and Decision Sciences, Oct. 1978, pp. 241-252.

J. L. Sweeney, "Effects of Federal Policies on Gasoline Consumption," Foresight: The Economic Impact of Energy Conservation, 3, Library of Congress, 201-225 (Dec. 1978).

J. L. Sweeney, "New Car Efficiency Standards and the Demand for Gasoline," Advances in the Economics of Energy and Resources: The Structure of Energy Markets, 1. R. Pindyck, editor. Greenwich, Conn.: JAI Press, 1979, pp. 105-133.

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- J. L. Sweeney, "Energy Problems and Policies," in The Economy in the 1980's: A Program for Growth and Stability, M. Boskin, editor. Institute for Contemporary Studies, San Francisco, Spring, 1980, pp. 353-392.
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- J. L. Sweeney, "The Relationship between Energy Use and the Economy," Energy Independence for the United States, N. M. Kamrany, editor. The Newport Foundation, 1981. Also published in U.S. Options for Energy Independence, N. M. Kamrany, editor. D. C. Hewath, 1982.
- J. L. Sweeney, "Resource Depletion, Research and Development, and the Social Rate of Discount: A Commentary and Extension," The Rate of Return for energy Investment, R. Lind and M. Greenberger, editors. Forthcoming.