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ANNUAL HIGHLIGHTS OF PROGRAMS IN ENERGY SCIENCES

MASTER

December 1978

DEPARTMENT OF ENERGY AND ENVIRONMENT

BROOKHAVEN NATIONAL LABORATORY
ASSOCIATED UNIVERSITIES, INC.

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DEPARTMENT OF ENERGY AND ENVIRONMENT

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UPTON, NEW YORK 11973

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PREFACE

The principal function of this report is to present an inventory and brief overview of the research programs carried out in the Energy Sciences area of the BNL Department of Energy and Environment. More complete and extensive descriptions of these programs are given in other documents, including a companion report Abstracts of Reports Published in Energy Sciences Programs (BNL 50972).

In order to present the reader with something more than just a statement of recent past accomplishments, each program description includes a statement of activities planned for the coming year. Thus some sense of direction is indicated for each program, and, in the aggregate, for the Energy Sciences area of the Department.

Meyer Steinberg and Masaki Suenaga provided full and prompt cooperation in the compilation of this report, and, a number of secretaries contributed to its production, particularly Lois Arns, Sharon Creveling, Ruth Duffy, Toni Fridae, Karen Kalish, and Pat Taylor.

INTRODUCTION

The Energy Sciences activities of the BNL Department of Energy and Environment have as their ultimate objective the development of an understanding of the chemical, physical, material, and process phenomena basic to many energy technologies encompassed by DOE's programs. In pursuit of this objective, activities are programmatically grouped within three Divisions: Chemical Sciences, Metallurgy and Materials Science, and Process Sciences. The Divisions are primarily administrative structures that provide greater cohesion and guidance to activities naturally sharing common scientific approaches to specific problems. Each Division can be characterized by its main focus: basic chemistry in the Chemical Sciences Division; basic and applied materials research in the Metallurgy and Materials Science Division; and applied chemistry and chemical engineering in the Process Sciences Division.

The free flow of ideas and information across these dividing lines is fostered. A number of complementary and interrelated programmatic interests can be found not only among programs within a Division but also among the Divisions comprising the Energy Sciences area.

Within the Department, the Energy Sciences activities represent the basic research efforts, excluding environmental research, and much of the applied chemistry and chemical engineering work. Work performed in the Energy Sciences area is expected to lead to the identification of ideas appropriate for further development in either the Energy Technology area of the Department or by other Departments of the Laboratory. Examples of such movement from the basic and applied areas to the development stage are (1) basic research on the chemistry of metal hydrides leading to the application of metal hydride beds for hydrogen storage; (2) basic research on superconductivity and applied research on superconductor tape fabrication leading to participation in a joint program on ac superconducting power transmission; and (3) applied research on polymer-impregnated concrete leading to a development program on the use of this material for highway service and geothermal well applications.

The formal organizational relationships among the Divisions of the Energy Sciences area and among the other areas of the Department are shown in the accompanying organization chart.

The purpose of this report is to present an overview of all the programs in the Energy Sciences area that were current in calendar year 1978. The objective and scope of each program is given, significant accomplishments for CY 1978 are summarized, and the principal activities planned for CY 1979 are briefly described. The publications issuing from these programs are cited in a companion document, Abstracts of Reports Published in Energy Sciences Programs (BNL 50972).

The programs being proposed for initiation in FY 1980 are listed at the end of each section.

DEPARTMENT OF ENERGY AND ENVIRONMENT BROOKHAVEN NATIONAL LABORATORY

HIGHLIGHTS OF 1978

A number of achievements in the Energy Sciences programs are of sufficient significance--either scientifically or technically--to be singled out and highlighted.

o It was postulated (on the basis of work done here and corroborating evidence adduced elsewhere) that the two photosystems operating in algae and green plants to reduce carbon dioxide and oxidize water have parallel initial charge separation steps:

Such a mechanism represents a significantly more efficient conversion of light energy into chemical energy than previously assumed and yields strong reductants to drive the biochemistry of both systems.

o The x-ray structure of 2,3,7,8-tetrahydro- $\alpha,\beta,\gamma,\delta$ -tetraphenylporphyrinatopyridine Zn(II), a model isobacteriochlorin, was determined. The resulting structure confirms the structure of isobacteriochlorins previously assumed on the basis of less direct evidence.

o An investigation of a simple photovoltaic cell based on porphyrin films showed an energy efficiency (generated power/incident power) as high as 2% for monochromatic light (420 nm) with magnesium porphyrin.

o Magnesium octaethylporphyrin bound in a synthetic hydrocarbon membrane acts as a photoamplifier in the sense that, for a single quantum of light absorbed by the porphyrin, many hydrogen (or hydroxide) ions are moved across the membrane.

o Careful analysis of the emissions from a spark-ignited internal combustion engine has clearly demonstrated that a significant amount of NO_2 has previously gone undetected primarily because of inappropriate sample drying techniques.

o A detailed study of the dehydrogenation of tetralin (a model compound for hydrogen-transfer systems used in coal conversion schemes) to naphthalene showed that in the vapor phase only one of the two possible isomers of the

intermediate dihydronaphthalene (the 1,2-dihydro isomer) is present in detectable quantities and that either tetralin or the dihydro intermediate must be present before hydrogen will add to naphthalene.

- o It has been shown that different methods of producing disorder--neutron, electron, or proton irradiation, deviations from stoichiometry, rapid quenching from high temperature, etc.--in A-15 intermetallic compound superconductors all result in essentially the same rate of change of critical properties with degree of disorder.

- o A systematic study of the strain dependence of the superconducting properties of several A-15 compounds showed that in V_3Ge strain increased the critical temperature although generally it has the opposite effect, and that strain could increase the ductility of Nb_3Sn and V_3Ge by a small but significant amount.

- o Determination of the detailed crystal structure of β -FeTi monohydride by neutron diffraction (in collaboration with the Chemistry Department) specified the locations of the hydrogen atoms and the lattice defect structures.

- o Most of the mechanical, physical, and electrical requirements for good dielectric insulation in ac superconducting power transmission cable service were shown to be simultaneously satisfied by laminated tapes made from biaxially oriented, very high modulus polypropylene film. In such tapes, the interlayer bond remains intact in liquid He, the loss tangent at 6 K is 20×10^{-6} , and, of particular importance, low temperature brittleness is eliminated.

- o A nondestructive x-ray method was developed for examining the taping patterns in cables. Originally developed to monitor the precision with which dielectric tapes are applied on experimental cables, the method has found extensive application as a means of studying degradation and damage in conventional cables in service.

- o It has been demonstrated that as much as 50 wt % of CO or 70 wt % of SO_2 can be copolymerized with ethylene monomer to form polyketone or polysulfone polymers, respectively. This process has the potential of conserving large quantities of ethylene feedstock and also utilizing large amounts of low cost fuel, such as CO, by-product and a waste product, such as SO_2 .

o Under Federal Highway Administration auspices, polymer concrete overlays for bridge deck applications were developed.

o As much as 80% of the carbon in lignite coal was converted to liquid and gaseous fuel products in a versatile tubular reactor pilot plant facility for studying the flash hydrolysis process.

CHEMICAL SCIENCES DIVISION

Donald J. Metz

The programs of the Chemical Sciences Division focus on understanding of chemical and physical phenomena basic to the energy technologies of DOE. The processes to which its present studies are relevant include conversion of solar energy to chemical and/or electrical energy and subsequent storage; coal gasification or liquefaction; use of hydrogen for energy storage; combustion of liquid and gaseous fuels; fuel recovery and separation of hazardous wastes; nitrogen fixation; advanced battery development; and magnetic fusion energy.

The programs represent a broad spectrum both of subjects and of investigative approaches. All emphasize the systematic acquisition of high quality scientific data, directed toward one or both of the following goals:

(1) developing basic understanding of phenomena and mechanisms, gaining new insights, and establishing new concepts regarding chemical reactions pertinent to energy-related programs; and (2) developing reliable techniques applicable to systems of concern in energy generation, conversion, or storage and in the control of the processes involved.

These programs are briefly described below. The program on Chemistry and Physics of Coal Utilization underwent major restructuring during the year, primarily because of reassignment of personnel and reallocation of funds. Three new programs were initiated in October 1978: Catalysis; Trace Element Analysis Using Synchrotron Radiation; and The Rotating Fluidized Bed Combustor.

PORPHYRIN CHEMISTRY

FY 1978: \$403,000

Principal Investigator: J. Fajer

FY 1979: \$423,000

Sponsor: Basic Energy Sciences (DOE)

Objective:

The objective of this study is to understand the mechanisms of porphyrin-mediated biochemical catalytic processes, with particular emphasis on photosynthesis, photocatalysis, and enzymatic reactions. The ultimate goal is to provide sufficient information to construct synthetic devices that mimic or improve upon the naturally occurring energy-conversion processes.

Scope:

Porphyrins are organometallic compounds that play indispensable roles in biochemical energy-conversion processes. The porphyrins function catalytically in these reactions, i.e., they are not consumed by the energy-producing process in which they participate. This work represents a multidisciplinary program that involves synthetic, structural, theoretical, and physical chemistry, and it encompasses (1) determination of the electronic structure and chemical properties of porphyrins and their radicals; (2) identification of the biological role of porphyrin ions in photosynthetic and metabolic reactions; and (3) applications of these catalytic reactions to energy-conversion systems such as production of electricity from solar energy by photoexcitation of porphyrins deposited on solid interfaces or isolated in micelles, production of hydrogen and/or oxygen in solution by using porphyrins to mimic the photosynthetic cell and photodecompose water, and fixation of nitrogen photochemically via porphyrin derivatives. Step (3) would thus allow direct production of energy via the catalyzed photolysis of water to form a fuel cell, or storage of energy in the form of metal hydrides to be used as a source of hydrogen fuel and in the form of nitrogen derivatives to be used as fertilizer.

The techniques for studying these reactions, which involve oxidation-reduction mechanisms, include optical and photoacoustic spectroscopy, electron spin resonance (esr), nuclear magnetic resonance (nmr), and electron nuclear double resonance (endor). The redox reactions are induced chemically, photochemically, and electrochemically, and the chemistry is guided by structural determinations and theoretical calculations used to

predict the chemical properties of the model systems. These, in turn, are used to establish the role of the porphyrins in biochemical catalysis.

Significant Accomplishments in 1978:

1. A new model was proposed for the electron transport chain in green plant photosynthesis. The first reduced chemical products induced by light in green plants are proposed to be the anions of pheophytin in photosystem II (PS II, the oxygen-evolving apparatus) and chlorophyll in photosystem I. (PS I, the system that reduces carbon dioxide). Such a mechanism represents a significantly more efficient conversion of incident light into chemical energy than previously postulated and yields strong reductants to drive the biochemistry of both systems. In addition, comparison of recently obtained data on the properties of chlorophyll in vitro with the optical, redox, and magnetic characteristics attributed to P680, the photoactive primary electron donor of PS I, led to the suggestion that P680 is a monomeric chlorophyll molecule complexed by its protein environment. This mechanism provides a reasonable explanation for the differing functions of chlorophylls in PS I and II. The primary donor of PS I is a dimer of chlorophyll, whereas that of PS II is a monomer. Additional support for the mechanisms proposed was found in in vitro systems designed to mimic the photosynthetic apparatus. Co-facial diporphyrins covalently linked ~4 angstroms apart were synthesized as models of the chlorophylls and pheophytins found in vivo. Laser flash photolysis (carried out in collaboration with T. Netzel of the BNL Chemistry Department) indicated that separation into charged species could be photo-induced within 7 picoseconds and that recombination to the ground state occurred in a few nanoseconds as observed in bacterial photosynthesis.

2. The photoelectrochemical properties of thin films of porphyrins were investigated in Al/porphyrin/Ag and Al/porphyrin/ $\text{Fe}(\text{CN})_6^{-3}$, $\text{Fe}(\text{CN})_6^{-4}$ /Pt cells. Action spectra indicated that the photoactive region was the porphyrin-aluminum electrode. The dark current-voltage (I-V) characteristics of the cells resembled those of a metal-insulator-semiconductor diode and were attributed to an Al- Al_2O_3 -porphyrin interface in which the porphyrin acts as a p-type semiconductor and forms a Schottky barrier with the aluminum electrode. (Other metals of low work function such as chromium and titanium, and n-type titanium dioxide, also yielded photoactive junctions with the porphyrins.)

The physical and chemical properties of the porphyrins were systematically altered by varying the metal and organic framework. The photovoltaic behavior of mesotetraphenyl-, mesotetrapropyl-, and octaethyl-porphyrins, porphins, chlorins, co-facial diporphyrins, and mesoporphyrin esters was investigated. Peak quantum yields (calculated for short-circuit currents obtained on illumination through the semi-transparent aluminum electrode at the major absorption band of the porphyrins) ranged from 10^{-1} to 10^{-4} at wavelengths of 400 to 450 nm. Films prepared by rapid evaporation of concentrated porphyrin solutions were ~50% more effective than films prepared by sublimation. The latter were found to be microcrystalline by electron microscopy at 20,000-fold magnification. For a given ligand, quantum efficiencies of the photocurrents paralleled the first oxidation potential of the porphyrins: the more easily oxidized compounds exhibited the higher quantum yields. Power conversion efficiencies varied from 10^{-2} to 10^{-6} for monochromatic light with magnesium tetraphenylporphyrin and cadmium porphin yielding open circuit voltages of ~1 volt and ~1% power conversions.

3. Because porphyrins are prosthetic groups in many enzymes that carry out electron transport, peroxide decomposition, nitrite and sulfite reductions, methylations and photosynthesis, they offer the tantalizing prospects of being powerful catalysts in vitro. Besides nitrogen reductions (isobacteriochlorins), oxygen reduction (for fuel cells) and chemical synthesis are some aspects being considered. Manganese porphyrins can bind oxygen reversibly and are thus of interest for oxygen reduction. In collaboration with B. M. Hoffman (Northwestern University), the reactions of Mn porphyrins with oxygen have been investigated. The reaction, according to esr, optical, and molecular orbital calculations is best described formally as

Furthermore, the Hückel calculations indicate that oxygen is bound in a Griffith model, i.e., edge on, parallel to the porphyrin plane:

rather than in the usual Pauling model (end-on) found in iron and cobalt porphyrin:

These results suggest that Mn porphyrins may be good catalysts for oxygen reduction and are also of interest because of the required presence, but unassigned role, of manganese in photosynthetic oxygen evolution.

Porphyrins have been shown to catalyze the heterogeneous oxidative dehydrogenation of hydrocarbon, by J. Manassen's group at the Weissmann Institute. In collaboration with that group, the redox properties of heteroporphyrins in which the pyrrole nitrogens have been replaced by sulfur, selenium, and tellurium were investigated, and the anion and cation radicals generated were characterized by optical, esr, and molecular orbital calculations.

4. To predict chemical reactivities and to help interpret experimental optical and esr results, self-consistent field and extended Hückel molecular orbital calculations were carried out for anions, cations, and neutral species of heteroporphyrins (dithia- and diselenatetraphenylporphyrins), chlorophylls a and b, pheophytin a, bacteriochlorophylls a and b, chlorophylls and chlorins ligated with oxygen, nitrogen, and sulfur donors, isobacteriochlorins, and iron and manganese porphyrins.

Principal Activities Planned for 1979:

1. Modeling studies of photosystem II will concentrate on the mandatory role of manganese in oxygen evolution. Co-facial dimeric porphyrins will be investigated as photo- and electrocatalysts in water decomposition and in electrolytic oxygen reduction.

2. The interaction between known or postulated primary components in the photosynthetic electron transport chain will be modeled by using porphyrins linked together to form dimers, trimers, and tetramers as models of reaction-center chlorophylls and by coupling them to electron donors and acceptors to mimic radical-radical interactions in photosynthetic systems.

3. Energy migration, charge transfer and sensitizing mechanisms, redox potentials, and reactivities of excited states induced by high power lasers in fluid and solid states will be studied by steady-state and picosecond resolution techniques.

4. The porphyrins and their radicals characterized to date will be tested for reactions with small molecules such as O_2 , O_2^- , O_2^{2-} , O_3 , NO, NO_2 , NO_2^- , CO, SO_2 , SO_3 , SO_3^- for attack on the metal and porphyrin moiety as models of known enzyme reactions and of pollutant-induced damage.

5. Work will continue on a model for the action of nitrite and sulfite reductases, enzymes in which porphyrins, called sirohemes, mediate the multi-electron reductions of sulfur and nitrogen compounds. The nitrogen reduction is light-driven in green plants, which raises the possibility of developing an artificial nitrogen-fixing system based on photoreactions of porphyrins.

6. In the photovoltaic work, other electrode materials will be screened to improve the efficiency of the cells and to expand π - π interactions between the porphyrins for better electron and exciton transfer between the pigments. Tetrabenzporphyrins and other compounds with electron-rich substituents are promising candidates because they act as one-dimensional conductors. To further improve efficiency, construction of cells of two photoactive electrodes will be attempted, in which oxidation occurs at one electrode and reduction at the other.

7. Molecular orbital calculations will be carried out for iron, manganese, and ruthenium porphyrins, which are known to complex oxygen, and for enzyme models such as cytochrome P450, siroheme, catalase, peroxidase, and cytochrome oxidase.

Publications in 1978:

Journal Articles

Fajer, J., Davis, M. S., Brune, D. C., Forman, A., and Thornber, J. P. Optical and paramagnetic identification of a primary electron acceptor of bacterial photosynthesis. *J. Amer. Chem. Soc.* 100, 1918-1920 (1978).

Fujita, I., Davis, M. S., and Fajer, J. Anion radicals of pheophytin and chlorophyll a: Their role in the primary charge separations of plant photosynthesis. *J. Amer. Chem. Soc.* 100, 6280-6282 (1978).

Thornber, J. P., Dutton, P. L., Fajer, J., Forman, A., Holten, D., Olson, J. M., Parson, W. W., Prince, R. C., Tiede, D. M., and Windsor, M. W. Isolated photochemical reaction centers from bacteriochlorophyll b containing organisms. *Photosynthesis* 77, Proceedings of the IV International Congress on Photosynthesis, D. O. Hall, J. Coombo, and T. W. Goodwin, Eds., pp. 55-70, The Biochemical Society, London, 1978.

Hanson, L. K., Davis, M. S., Fujita, I., and Fajer, J. Molecular orbital calculations of chlorophylls and chlorins. *Biophys. J.* 21, 195a (1978); Presented at the Biophysical Society Meeting, Washington, D. C., March, 1978.

Fajer, J., Davis, M. S., Thornber, J. P., and Forman, A. Photosynthesis at 1000 nm. Porphyrim Chemistry Advances, F. R. Longo, Ed., pp. 89 - 108, Ann Arbor Science Publishers, Ann Arbor, Michigan, 1978.

Hanson, L. K. and Hoffman, B. M. Griffith model bonding in oxygen manganese porphyrins. *Biophys. J.* (in press).

Davis, M. S., Forman, A., Hanson, L. K., and Fajer, J. Ligated chlorophylls as primary donors in photosynthetic oxygen evolution. *Biophys. J.* (in press).

Kampas, F. J., Yamashita, K., Chang, C. K., and Fajer, J. Photoelectrochemical properties of metalloporphyrins. *J. Electrochem. Soc.* (submitted).

Oral Presentations

Kampas, F. J. and Fajer, J. Photoelectrical properties of porphyrins, chlorins and bacteriochlorins. Presented at the 13th Informal Conf. on Photochemistry, Clearwater, Florida, January, 1978.

Davis, M. S., Forman, A., Spaulding, L. D., and Fajer, J. Chlorin models of the chlorophylls of photosystems I and II. Presented at the 175th National Meeting of the Amer. Chem. Soc., Anaheim, Calif., March, 1978.

Fujita, I., Davis, M. S., Forman, A., Hanson, L. K., and Fajer, J. Anion radicals of chlorophyll and pheophytin. Presented at the 175th National Meeting of the Amer. Chem. Soc., Anaheim, Calif., March, 1978.

Fajer, J. An ESR visit to green plants. Presented at Gordon Conference on Magnetic Resonance in Biology and Medicine, Tilton, New Hampshire, July, 1978.

INVESTIGATION OF THE CHEMISTRY OF ENERGETIC COMPOUNDS

FY 1978: \$170,000

Principal Investigator: M. Hillman

FY 1979: \$165,000

Sponsor: Basic Energy Sciences (DOE)

Objective:

The objective of this study is to prepare and characterize classes of organic compounds that potentially have interesting properties as catalysts, photocatalysts, conductors, photoconductors, and possibly superconductors.

Scope:

The preparation, structure, and chemistry of energetic compounds are being investigated. Energetic compounds may undergo certain types of reactions that ordinary compounds will not, for example, they may have the ability to catalyze other reactions or to become electrical conductors under the influence of light. In the area of catalysis, this project is related to the possibility of fixation of nitrogen. In the area of conductivity, it is related to the possibilities of both photoconductivity and superconductivity in organic molecules. Heretofore, all work on organic superconductors has involved linear arrays of molecules. Present theory suggests that superconductivity in linear arrays is virtually impossible. The work in this project is directed toward the possibility of preparing three-dimensional arrays that are potential conductors, which would have structures similar to those of known inorganic superconductors. Of particular interest are intensely colored derivatives of compounds known to have some degree of conductivity. Incorporation of certain molecules, such as ferrocene derivatives, can enhance the conductivity of membranes. Incorporation of photoconducting molecules in membranes may prove of practical interest in developing uses of solar energy.

Significant Accomplishments in 1978:

1. The hydrogenation of 1,1',3,3'-bis(tetramethylene)ferrocene was successfully accomplished; this is a step toward the goal of hydrogenating a bridged ferrocene with enough bridges to trap an iron atom.
2. The hydrogenation of 1,1',2,2',4,4'-tris(trimethylene)ferrocene did not lead to the product desired. Instead a bridge opened and 4-(n-propyl)-1,1',2,2'-bis(trimethylene)ferrocene was formed. This was attributed to

strain in the molecule which is expected to be absent in compounds with four-carbon bridges. Other products obtained under conditions related to those of the hydrogenation reaction were 3-trifluoroacetyl-1,1',2,2',4,4'-tris(trimethylene)ferrocene, 1,1',3,3',4,5-tris(trimethylene)ferrocene, and di[1,1',2,2',4,4'-tris(trimethylene)ferrocene-12-yl] oxide.

3. In four compounds for which both the Mössbauer parameters and the crystal structures were known, a strong correlation was found between the Mössbauer parameters and the iron-to-ring distances in the molecules. Similar compounds for which the crystal structures were not known but the iron-to-ring distances were assumed to be the same as in the measured compounds with the same bridge structure, also fit the correlation.

Principal Activities Planned for 1979:

1. The preparation of multibridged tetra- and pentamethyleneferrocenes will be carried forward, it is hoped, to the completely bridged compounds.
2. Hydrogenation studies on these compounds will continue.

Publications in 1978:

Journal Articles

Hillman, M., Gordon, B., Weiss, A. J., and Guzikowski, A. P. Bridged ferrocenes. I. J. Organometallic Chem. 155, 77 (1978).

Hillman, M. and Fujita, E. Bridged ferrocenes. II. The crystal and molecular structure of 1,1',2,2',4,4'-tris(trimethylene)ferrocene. J. Organometallic Chem. 155, 87 (1978).

Hillman, M. and Fujita, E. Bridged ferrocenes. III. The crystal and molecular structure of 1,1',2,2',3,4,4',5'-tetrakis(trimethylene)ferrocene. J. Organometallic Chem. 155, 99 (1978).

Spaulding, L. D., Williams, G. J. B., and Hillman, M. Bridged ferrocenes. IV. The crystal and molecular structure of 1,1',2,2',3,3',4,5,4',5'-pentakis(trimethylene)ferrocene. J. Organometallic Chem. 155, 109 (1978).

Oral Presentations:

Hillman, M., Gordon, B., Weiss, A. J., and Fajer, R. Hydrogenation of bridged ferrocene derivatives. Presented at American Chemical Society Meeting, Anaheim, Calif., March, 1978.

KINETICS AND MECHANISMS OF CHEMICAL PROCESSES RELATED TO
THE DEVELOPMENT AND USE OF ENERGY

FY 1978: \$160,000

Principal Investigator: J.W. Sutherland

FY 1979: \$170,000

Sponsor: Basic Energy Sciences (DOE)

Objective:

The objective of this program is to obtain basic kinetic and mechanistic information about selected chemical systems associated with the development and use of energy sources for which present data are inadequate or unavailable.

Scope:

The reactivity of sulfur dioxide and of transient intermediate nitrogen compounds is being investigated. The photochemistry of selected molecules adsorbed on high surface area solids is also being studied.

The results of the investigation, in addition to their intrinsic value to the general field of chemical kinetics, are available as quantitative input data for energy models designed to assess the relative impacts of using various energy sources. Flash photolytic and pulse radiolytic techniques are used to characterize short-lived transient chemical species, and steady-state photolytic, steady-state radiolytic, and standard kinetic techniques are used to identify and measure yields of final products of a particular overall reaction. Information developed in this program is relevant to problems in sulfur chemistry associated with the development and use of geothermal energy sources and of fossil fuels. It is also pertinent to investigations into methods for nitrogen fixation and into systems being considered for the photochemical conversion and storage of solar energy.

Significant Accomplishments in 1978:

1. Extensive computations showed that the proposed model accounted satisfactorily for the processes involved in the formation, growth, and loss of the H_2SO_4 aerosol produced on flash photolysis of SO_2 /gas mixtures.
2. More detailed kinetic analysis was carried out on the catalytic oxidation of SO_2 in aqueous solution. The spectrum and an association constant of an unstable Fe(III)-S(IV) complex were measured.
3. A study of the oxidation of hydrazine in aqueous solution showed that a transient adduct was not formed when hydroxyl radicals reacted with the hydrazine.

4. The flash photolytic technique was applied successfully to the study of the photochemistry of pyrene physically adsorbed on a porous glass of high surface area.

Principal Activities Planned for 1979:

1. Additional computational and experimental work will be done to further test the proposed kinetic model for the catalytic oxidation of SO_2 in aqueous solution.

2. The transient species and permanent products formed on the flash and steady-state photolysis of hydrazine in non-aqueous solvents will be investigated.

3. The photolysis of pyrene adsorbed on porous glass will be carried out by using a pulsed laser in addition to the currently available techniques in order to elucidate more details concerning the photophysical and photochemical processes occurring at shorter time scales.

Publications in 1978:

Journal Articles

Fogel, L. D. and Sutherland, J. W. Aerosol formation on the flash photolysis of SO_2 /gas mixtures. J. Chem. Phys. (in press); Presented at the 175th Meeting of the American Chemical Society, Miami Beach, Florida, September, 1978.

Sutherland, J. W. Pulse radiolysis of aqueous hydrazine solutions. The triazene species. J. Phys. Chem. (in press).

Piciulo, P. L. and Sutherland, J. W. Flash photolysis in the adsorbed state: Pyrene on porous glass. J. Amer. Chem. Soc. (submitted).

COMBUSTION STUDIES ON ALTERNATIVE FUELS

FY 1978: \$242,000

Principal Investigator: R. B. Klemm

FY 1979: \$255,000

Sponsor: Basic Energy Sciences (DOE)

Objective

The objective of this study is to provide information on and an understanding of the combustion of alternative fuels (such as hydrocarbon liquids, methyl and ethyl alcohol, and hydrogen) in burners and engines. Of primary interest are the effects of combustor operating conditions and fuel parameters on the mechanisms of combustion, including combustion efficiency and product emissions.

Scope:

It has recently become necessary for the U.S. to consider the utilization of unconventional or alternative fuels such as solvent-refined coal and hydrogen, methanol, and synthetic gasoline derived from coal. In addressing some technical aspects of the alternative fuels question, such as combustion efficiency and pollutant emission rates, this program has one essential purpose, i.e., to investigate those alternative fuels that may be used to supplement or replace petroleum-derived fuels for operation in both stationary and mobile combustion devices. Particular emphasis is placed on the study of the kinetic and mechanistic factors in the combustion and pollutant formation processes to clarify the fundamental principles involved. A two-phase program has been established to accomplish these objectives. In the first phase, flat-flame burners and other devices are used to provide realistic test bases for measuring the effects of operating parameters, such as fuel type and air-fuel ratio, on the pressure, temperature, and concentration profiles for stable and transient species that exist during the combustion of various fuels. Because of the possibly significant role of elementary chemical reactions in determining observed combustion characteristics, the first-phase results plus data from other investigations are used to define the potential importance of specific reactions during combustion. In the second phase, the specific modes and rates of the indicated chemical reactions are determined in controlled and isolated experiments that eliminate the complexities of actual combustion devices. Ancillary combustion modeling studies are done to consolidate results.

Significant Accomplishments in 1978:

1. The discharge flow - resonance fluorescence reactor, built in 1977 was used in the measurement of rate coefficients for the reactions of oxygen atoms with methane, methanol, formaldehyde, acetaldehyde, and ethylene. Rate data for these reactions are summarized in the table below.

2. The flash photolysis experiment was also used to obtain absolute rate measurements for the O/CH_3CHO reaction, and a previous kinetic study of the O/H_2CO reaction was re-evaluated. The good agreement (see table) between the results of the two techniques for both these reactions enhances the reliability of these measurements.

3. The study of the formation of nitrogen oxides in a methanol-fueled spark-ignited engine, begun in 1977, was extended. Exhaust gas samples were withdrawn from within 1/4 in. of the engine exhaust valve, and losses and conversions of NO and NO_2 were thoroughly tested. The results showed conclusively that NO_2 represented the largest fraction of NO_x ($NO + NO_2$) under lean burn conditions, and that this NO_2 was emitted directly from the engine cylinder.

Rate Data for Reactions of $O(^3P)$

Reactant	$k_{298} \times 10^3$ ($cm^3 s^{-1}$)	$A \times 10^{11}$ ($cm^3 s^{-1}$)	E_a (cal/mole)	T (K)	Method
CH_4	-----	$4.79 \pm .80$	9110 ± 650	548-753	DF-RF
CH_3OH	0.092 ± 0.011	12.3 ± 2.3	5690 ± 250	299-765	DF-RF
H_2CO	1.50 ± 0.10	$2.9 \pm .5$	3065 ± 95	298-746	DF-RF
CH_3CHO	$5.27 \pm .50$	$1.62 \pm .15$	2031 ± 75	298-755	DF-RF
C_2H_4	9.88 ± 1.05	$0.87 \pm .08$	1300 ± 90	298-746	DF-RF
H_2CO	$1.61 \pm .17$	$2.78 \pm .32$	3030 ± 80	250-498	FP-RF
CH_3CHO	$5.30 \pm .60$	$1.43 \pm .30$	1960 ± 100	298-507	FP-RF

$k(T) = A \exp(-E_a/RT)$; error limits are 2 x std. dev.

Principal Activities Planned for 1979:

1. The discharge flow - resonance fluorescence apparatus will be equipped with a quartz tube and high temperature furnace to extend its range

to >1200 K. Rate parameters for O atom reactions with alkanes and alcohols such as ethane, propane, butane, and ethanol will be measured. Kinetic studies of the reactions of H atoms and N atoms with some of the same compounds are planned.

2. A high temperature all-quartz reaction cell will be designed so that kinetic studies of OH radical reactions can be performed in the flash photolysis - resonance fluorescence apparatus at elevated temperatures.

3. Studies on a cooled, porous plate, flat-flame burner will be initiated and will be coordinated with the development of a photoionization mass spectrometer (PIMS) in a joint effort between the Chemistry Department and the Department of Energy and Environment. Among other applications of the PIMS experiment will be use of vacuum UV radiation from the National Synchrotron Light Source for selective photoionization of species in gaseous samples probed from flames.

Publications in 1978:

Journal Articles

Klemm, R. B. Absolute rate parameters for the reactions of formaldehyde with O-atoms and H-atoms over the temperature range 250 to 500°K. J. Chem. Phys. (submitted).

Klemm, R. B. and Skolnik, E. G. Absolute rate parameters for the reactions of atomic oxygen with methane and methanol. J. Chem. Phys. (submitted).

BIOELECTROCHEMISTRY AND ELECTROCHEMISTRY

FY 1978: \$150,000

Principal Investigator: S. W. Feldberg

FY 1979: \$155,000

Sponsor: Basic Energy Sciences (DOE)

Objective:

The objective of this study is an understanding of the mechanism of conversion of light energy to chemical energy in biological systems, specifically that part of the process involving the transport of an electron across a membrane-water interface and across the entire membrane. An understanding of this process will facilitate the successful construction of artificial photosynthetic devices.

Scope:

The major area of interest is the study of the kinetics and mechanisms of electron transfer between (photo) excited states of molecules (porphyrins, for example) bound to a bilayer lipid membrane (BLM) and acceptors or donors located either in the aqueous phases or within the BLM. A general objective of having reactants in two different phases, or immobilized within a phase, is to separate the photogenerated products and preclude the back reaction. It is hoped that the reaction products can perform some useful function, e.g., create a voltage that drives other ions across a membrane or modifies membrane transport properties; cause an electric current to flow through electrodes; lead to redox changes that produce pH changes or "energized" species (ATP). A specific aim of these studies is to characterize these processes: are these reactions, for example, governed by the same factors that control homogeneous chemical reactions? The role of diffusion in bringing reactants to a photo-activated surface is being studied theoretically and experimentally. Diffusion effects provide additional information for quantitating surface density of excited states and excited-state products.

Significant Accomplishments in 1978:

It has been demonstrated that photogenerated membrane-bound magnesium octaethylporphyrin cation (MgOEP^+) selectively mediates the transport of hydrogen ion and hydroxide across a lipid bilayer membrane, by a mechanism known as "carrier" transport. The photogenerated MgOEP^+ cation is probably hydrated (at the Mg atom). In the presence of an electric field the

$\text{H}_2\text{O-MgOEP}^+$ moves across the membrane. There is a chemical equilibrium between this species and the neutral HO-MgOEP , which can drift back across the membrane, and recombine with a hydrogen ion, H^+ , to re-form the $\text{H}_2\text{O-MgOEP}^+$. The net result is the transport of hydrogen ions from one side of the bilayer to the other. Such a mechanism has some interesting implications: it can act as a photo-amplifier in the sense that a single absorbed photon can produce a $\text{H}_2\text{O-MgOEP}^+$ cation which in turn can carry many hydrogen ions across the membrane; under special conditions, such that there is an electron acceptor on one side of the membrane and an electron donor on the other, continuous light could "pump" hydrogen ions from one side of the bilayer to the other.

Principal Activities Planned for 1979:

The incorporation of other porphyrins (metallo- or free base) into the membrane will be pursued. The objectives are to elucidate the role of the excited singlet and triplet states in the redox processes, the role of the central metal atom in the carrier transport mechanism previously discussed, and the possibility of energy transfer between different porphyrins in the bilayer. Some of these phenomena will be investigated by using optical techniques with vesicles (spherical bilayers). The experimental apparatus is under construction.

Publications in 1978:

Journal Articles

Andersen, O. S., Feldberg, S., Nakadomari, H., Levy, S. and McLaughlin, S. Electrostatic interactions among hydrophobic ions in lipid bilayer membranes. *Biophysical Journal* 21, 35-70 (1978).

Feldberg, S. W. and Delgado, A. B. Inner voltage clamping: A method for studying interactions among hydrophobic ions in a lipid bilayer. *Biophysical Journal* 21, 71-86 (1978).

Young, R. C. and Feldberg, S. W. Photo-initiated mediated transport of H_3O^+ and/or OH^- across GMO bilayers doped with magnesium octaethylporphyrin. *Biophysical Journal* (submitted).

Young, R. C., Smalley, J. F. and Feldberg, S. W. The kinetics of photo-initiated porphyrin-mediated transport of H_3O^+ and/or OH^- across a bilayer lipid membrane. *Biophysical Journal* (submitted).

MOLECULAR STRUCTURE OF PORPHYRINS AND
PHOTO-ENERGY TRANSDUCING SYSTEMS

FY 1978: \$70,000

Principal Investigator: J. Fajer

FY 1979: \$40,000

Sponsor: Basic Energy Sciences (DOE)

Objective:

The objectives of this work are to provide the structure-function and structure-reactivity correlations for compounds considered as potential energy transducers in photochemical and catalytic redox reactions.

Scope:

The compounds of principal interest are oxidized, reduced, and neutral chlorins and bacteriochlorins; porphyrins, especially those containing multivalent transition metals; and dimeric and polymeric porphyrin derivatives in crystalline or monolayer arrays, which can serve as models of photosynthetic, enzymatic, and catalytic biological reactions. Such synthetic models offer the chemical malleability and stability required for detailed structural determinations often unavailable in naturally occurring compounds. Accurate molecular and spatial structures for current models are required to guide theoretical calculations, explain mechanisms of electron transfer and radical-radical interactions, and help interpret electron spin resonance, nuclear magnetic resonance, and resonance Raman results. The techniques used include x-ray and neutron diffraction, extended x-ray absorption fine structure (EXAFS), photoacoustic spectroscopy, and polarized microspectrophotometry.

Significant Accomplishments in 1978:

1. The structure of $\alpha,\beta,\gamma,\sigma$ -tetra-n-propylporphyrinato lead II was determined by x-ray diffraction. Lead porphyrins are particularly susceptible to demetallation under mild hydrolytic or photolytic conditions. The x-ray results confirm that the lead atom is located a large distance out of the porphyrin plane. The weak lead-nitrogen bonds thus explain the photochemistry and lability of the complex.

2. Synchrotron radiation provides a high intensity source of x-rays which can be used to probe the environment of the metal atom in organometallic compounds. Powder samples of iron u-oxo-tetraphenylporphyrin, $(\text{FeTPP})_2\text{O}$,

zinc tetraphenylporphyrin, (ZnTPP), and their oxidized salts $(\text{FeTPP})_2\text{O}^+\text{ClO}_4^-$ and $\text{ZnTPP}^+\text{ClO}_4^-$ were investigated by extended x-ray absorption fine structure (EXAFS) as models of porphyrin prosthetic groups in enzymatic and photosynthetic systems. Notable changes were found between the iron compound and its salt, in which oxidation had occurred at the metal site, without the need for extensive theoretical analysis of the data. The EXAFS results for the zinc compounds were consistent with electron spin resonance and x-ray data which showed that oxidation occurred by loss of an electron from the porphyrin π network and resulted in only small changes in bond distances.

Principal Activities Planned for 1979:

1. Work will be concentrated on growing crystals of monomers and dimers, as well as oxidized and reduced chlorins and bacteriochlorins, as models of the transients observed in the picosecond conversion of light into chemical energy.
2. To avoid the difficulties of growing single crystals of very reactive compounds large enough for x-ray or neutron diffraction, polarized single-crystal absorption microscopy and EXAFS studies will be used to probe changes in oxidation states and effects of axial ligands in chlorins, porphyrins, and isobacteriochlorins as models, which should eventually allow direct measurements of in vivo systems.
3. Sublimed and evaporated thin films of porphyrins yield markedly different photovoltaic responses in photoelectrochemical cells. The morphology of these thin films will be investigated by EXAFS, low-angle x-ray scattering, and scanning electron microscopy.

Publications in 1978:

None.

METAL HYDRIDES

FY 1978: \$282,000

Principal Investigators: R. H. Wiswall
J. J. Reilly

FY 1979: \$280,000

Sponsor: Basic Energy Sciences (DOE)

Objective:

The objective of this study is an understanding of the basic chemistry and physics of metal-hydrogen systems. Metal hydrides comprise a class of compounds of intrinsic scientific interest, and certain ones already have potentially interesting applications in such energy-related fields as hydrogen storage, isotope separation, and tritium scavenging.

Scope:

The storage of hydrogen in the form of solid metal hydrides promises to be important in the energy economy of the future. As a fuel, hydrogen has the advantages of being both non-polluting and easily interconvertible with other forms of energy. Its storage problems have been partially solved by the development of new alloy hydrides. Further improvements will be fostered by an increased understanding of the basic chemistry and physics of metal-hydrogen systems, which is the long-range goal of this program. The experimental approaches include determination of pressure-temperature-composition relationships in selected metal-hydrogen systems for use in calculating thermodynamic properties; establishment of crystal structures in metal-hydrogen systems by means of x-ray and neutron diffraction; measurement of reaction rates in such systems; and studies of the structure and properties, including catalysis, of hydride surfaces.

Hydrides also have potential value as components of processes for deuterium production or tritium scavenging. Here too basic data are required on the equilibria and kinetics of gas-solid exchange reactions involving the pertinent isotopes, and correlations between isotopic and other properties of alloy-hydrogen systems need to be developed.

Significant Accomplishments in 1978:

1. A study of the system $\text{TiCr}_{1.8}\text{-H}_2$ revealed several unusual features. The two closely related crystal forms of the intermetallic compound yield hydrides of very different stabilities; one of the forms took up hydrogen to

$H/n = 1.3$ without change of symmetry; and the partial molar volume of H in the metal was only 1.0 cm^3 .

2. In β -titanium, analysis of P-T-C data, corrected to conditions of constant volume, showed the H-H interaction to be attractive, in contrast to the cases of vanadium and palladium.

3. The crystal structures of several hydrides and deuterides of V, Nb, and Ta were determined by neutron diffraction, and the mechanism of a phase transition in $\text{TaD}_{0.77}$ was established.

4. Apparatus was built in which the surface activity of metal hydrides could be studied, and equipment for sensitive determination of the magnetic susceptibility of solid samples was assembled and operated.

Principal Activities Planned for 1979:

1. Studies of the system $\text{TiCr}_{1.8}\text{-H}_2$ will be completed, including a comparison of deuterium with hydrogen isotherms on both forms and further determinations of partial molar volumes. A similar study on the two forms of TaV_2 , already begun, will be completed.

2. P-T-C data will be obtained on the low hydrogen region of alloy-hydrogen systems, with the aim of deriving H-H interactions and the non-configurational part of the partial molar entropy of hydrogen. This should shed light on the constitution of these solids.

3. Neutron diffraction studies of hydride structures will continue, with emphasis on Group V metals and $\text{TiCr}_{1.8}$.

Publications in 1978:

Journal Articles

Lynch, J. F., Reilly, J. J., and Tanaka, J. The titanium-molybdenum-hydrogen system: Isotope effects, thermodynamics and phase changes. Transition Metal Hydrides, Robert Bau, Ed., pp. 342-365, American Chemical Society, 1978.

Rudman, P. R., Reilly, J. J., and Wiswall, R. H. The formation of metastable hydrides $\text{Ti}_{.75}\text{Al}_{.25}\text{H}_x$, $x < 1.5$. J. Less-Common Metals **58**, 231 (1978).

Reilly, J. J. Synthesis and properties of useful metal hydrides. Hydrides for Energy Storage, A. F. Andresen and A. J. Maeland, Eds., pp. 301-322, Pergamon Press, 1978.

Reilly, J. J. Applications of metal hydrides. Hydrides for Energy Storage, A. F. Andresen and A. J. Maeland, Eds., pp. 527-550, Pergamon Press, 1978.

Lynch, J. F., Reilly, J. J., and Millot, F. The absorption of hydrogen by binary vanadium-chromium alloys. *J. Phys. Chem. Solids* 39, 883 (1978).

Reilly, J. J. Metal hydrides and energy storage. *Bull. Amer. Phys. Soc.* 23(3), 295 (1978).

Thompson, P., Pick, M. A., Reidinger, F., Corliss, L. M., Hastings, J. M., and Reilly, J. J. Neutron diffraction study of β iron titanium deuteride. *J. Phys. F: Metal Phys.* 8, L75 (1978).

Shapiro, S. M. and Reidinger, F. Neutron scattering studies of superionic conductors. *Physics of Superionic Conductors*, M. B. Salomon, Ed. (in press).

Wiswall, R. Hydrogen storage in metals. *Hydrogen in Metals II*, G. Alefeld and J. Voelkl, Eds., pp. 201-242, Springer-Verlag, December 1978.

Reidinger, F., Reilly, J. J., and Stoenner, R. W. Single crystal preparation and characterization of Group VA metal hydrides. *J. Less-Common Metals* (in press).

Thompson, P., Reilly, J. J., Reidinger, F., Hastings, J. M., and Corliss, L. M. Neutron diffraction study of γ iron titanium deuteride. *J. Phys. F: Metal Phys.* (submitted).

Oral Presentations:

Lynch, James F. The solution of hydrogen in binary alloys: intermetallic compounds vs. random alloys. Presented at Albuquerque Hydride Meeting, Sandia Labs., Albuquerque, New Mexico, March 8 and 9, 1978.

Reilly, J. J. and Johnson, J. R. Synthesis, properties and applications of some useful metal hydrides. Presented at Albuquerque Hydride Meeting, Sandia Labs., Albuquerque, New Mexico, March 8 and 9, 1978.

Reidinger, F., Axe, J. D., Shapiro, S. M., and Wakabayashi, N. The superionic fluorite structure: a neutron diffraction study of PbF_2 and BaF_2 . Presented at 36th Annual Pittsburgh Diffraction Conference, Pittsburgh, Pa., October 26-27, 1978.

Reidinger, F., Reilly, J. J., and Stoenner, R. W. Single-crystal neutron diffraction studies of group VA metal hydrides (deuterides). Presented at 36th Annual Pittsburgh Diffraction Conference, Pittsburgh, Pa., October 26-27, 1978.

CHEMISTRY AND PHYSICS OF COAL UTILIZATION

FY 1978: \$223,000

Principal Investigator: T. Gangwer

FY 1979: \$102,000

Sponsor: Basic Energy Sciences (DOE)

Objective:

The objective of this program is to develop basic mechanistic information on the hydrogen-transfer chemical reactions that are fundamental to conversion of coal to liquids. The insight gained should contribute to an improved understanding of processing and product formation.

Scope:

The program is an investigation of hydrogen-transfer chemistry, which is the keystone of currently developing pilot plant liquefaction processes. The work is aimed at gaining kinetic and mechanistic insight into this complex chemistry by developing a sound understanding of the hydroaromatic donor-solvent reactions. The nature of the chemistry at phase interfaces (gas/solid/liquid), which occur in liquefaction processes, is being studied. The hydrogen-transfer catalytic activities of minerals common to coal are being investigated. The hydrogen transfer by donor solvents to model compounds is being studied to determine the detailed mechanistic pathways that give rise to products.

Significant Accomplishments in 1978:

1. The gas phase mechanism and kinetics for tetralin dehydrogenation were determined at 400°C. This tetralin/1,2 dihydronaphthalene/naphthalene system follows a heterogeneous, zero-order mechanism.
2. The condensed phase mechanism and kinetics for tetralin dehydrogenation at 400°C were observed to follow a zero-order rate law. The pathway for the condensed phase reaction differs from that for the gas phase as evidenced by the formation of methylindane as a major product and the absence of dihydronaphthalene in the condensed phase.
3. The catalytic and reactive site activities of the major minerals common to coal were ranked on the basis of their influence on the tetralin gas phase system.
4. Annealing of coal minerals at 400°C was found to result in an increase in surface area but a decrease in catalytic activity toward

tetralin. X-ray and infrared analysis indicated that the loss in activity was not due to bulk chemical composition changes.

Principal Activities Planned for 1979:

1. The gas and liquid phase study of donor solvents will be expanded to other hydroaromatics, and the effect of added hydrogen gas on the mechanisms will be studied.

2. The kinetics of the coal mineral/hydroaromatic systems will be studied.

3. Model coal compounds will be added to the hydroaromatics systems and the resultant kinetics and mechanisms will be investigated.

Publications in 1978:

Journal Articles

Gangwer, T., Casano, S., and MacKenzie, D. A mechanistic study of the hydrogenation/dehydrogenation of some hydroaromatics. J. Phys. Chem. (submitted).

Gangwer, T. and Prasad, H. Hydrogen transfer catalytic activity of minerals common to coal. Fuel (submitted).

Oral Presentations

Gangwer, T. Hydrogen transfer mechanisms relevant to coal liquefaction. Informal presentation at Mobil Research & Development Corp., Princeton, New Jersey, December 15, 1978.

HIGH TEMPERATURE CHEMISTRY

FY 1978: \$175,000

Principal Investigator: J. J. Egan

FY 1979: \$238,000

Sponsor: Basic Energy Sciences (DOE)

Objective:

The objective of this study is to develop an understanding of the thermodynamic and transport properties of ionic crystals, molten salts, and solid and liquid alloys that are relevant to energy storage and conversion.

Scope:

In this program the thermodynamic and transport properties of substances at high temperatures are studied, and an attempt is made to explain the results in terms of appropriate atomic models. Electrochemical methods are stressed since they yield very accurate results and also have possible direct application to batteries, fuel cells, and solar cells, when new methods are developed. The techniques of solid state electrochemistry as well as high temperature calorimetry are employed. The movement of electrons and electron holes in both ionic crystals and molten salts is being examined in view of its fundamental importance and its potential applications. These include such diverse phenomena as battery self-discharge, development of new electrolytes for thermodynamic studies, and improvements in efficiency of production of metals by molten salt electrolytes. Substances of interest in this program include alloys that are semiconductors in the liquid and solid state with application to solar cells, solid and molten salt electrolytes with direct application to high energy batteries and fuel cells, and high temperature reactor fuels.

Significant Accomplishments in 1978:

1. The electronic conductivity and mobility of electrons in molten KCl and NaCl were measured. New methods for studying electronic conduction and transport properties of electrons in molten salts were developed.
2. Coulometric titrations were carried out on solid thin films using CaF_2 and BaF_2 solid electrolytes. Previously solid state titrations had been successful only with compounds having interdiffusion coefficients greater than $10^{-5} \text{ cm}^2/\text{sec}$. Results have now been obtained on intermetallic phases with much lower chemical diffusion coefficients. Systems studied include

Ca-Au, Ba-Au, Dy-Au, Na-Au, Mg-Sb, and Mg-Bi. Information was obtained on (1) phases previously unknown in some of the systems, (2) thermodynamic quantities unreported to date, (3) limits of stoichiometry, (4) conductivity, and (5) degree of disorder. High volatility of one of the components and electrolyte impurities limited the accuracy of the technique, but progress was made in eliminating these deficiencies.

3. Progress was made on the measurement and theory of the variation of conductivity of compound semiconductors with the thermodynamic activity of the components. In the case of liquid Na-Bi alloys, the activities of the components were determined, and conductivity measurements were initiated to test predictions.

Principal Activities Planned for 1979:

1. Construction and operation of a new high temperature calorimeter of the twin Calvet type, capable of operation up to temperatures of 1200°C, is underway. This calorimeter will be used to measure heats of mixing of liquid compound semiconductors. Results will be used to elucidate the relation between electron and electron-hole concentrations and the concentration of the component metals.

2. A new apparatus has been constructed to measure the electrical conductivity of liquid compound semiconductors in which one of the components is volatile. Measurements will be made on Na-Bi alloys and, if successful, extended to other systems.

3. Single crystals will be grown from a melt that has been pre-electrolyzed to eliminate traces of oxygen impurities. The crystals, predominantly fluorides, will be used as solid electrolytes.

4. Work will continue on the coulometric titration of solid thin films with concurrent measurements of the electrical conductivity so that the composition will be precisely controlled.

Publications in 1978:

Journal Articles

Delcet, J., Heus, R. J., and Egan, J. J. Electronic conductivity in solid CaF_2 at high temperatures. J. Electrochem. Soc. 125, 755 (1978).

Delcet, J. and Egan, J. J. Thermodynamics of liquid Ca-Ag and Ca-In alloys. J. Less-Common Met. 59, 229 (1978).

Delcet, J. and Egan, J. J. Thermodynamics of liquid Ca-Zn alloys.
Met. Trans. B 9B, 728 (1978).

Delcet, J. and Egan, J. J. Thermodynamics of dilute ternary Ca alloys.
Met. Trans. B (submitted).

Delcet, J. and Egan, J. J. Free energy of formation of CaC_2 . J. Chem.
Thermodynamics (submitted).

Davis, R. E., Heus, R. J., and Egan, J. J. Electronic conduction in molten
potassium chloride. J. Electrochem. Soc. (submitted); Presented at Electro-
chemical Society Meeting, Pittsburgh, Pa., October 1978.

Oral Presentations

Delcet, J. and Egan, J. J. Thermodynamics of liquid Ca-Au alloys. Pre-
sented at Electrochemical Society Meeting, Seattle, Wash., May 1978.

CATALYSIS

FY 1978: ---

Principal Investigator: R. S. Sapienza

FY 1979: \$65,000

Sponsor: Basic Energy Sciences (DOE)

Objective:

The goal of this investigation is to achieve an understanding of the mechanism(s) of carbon oxide reduction on metal and metal oxide surfaces.

Scope:

There is much controversy over the mechanism of the Fischer-Tropsch and related syntheses. A comparison of reaction results does not make it probable that basically different reaction schemes should be assumed for different catalysts. A unified picture capable of explaining or predicting catalyst behavior is needed to understand and improve these processes.

A novel concept is proposed -- that the Fischer-Tropsch reaction proceeds via the chemisorption of carbon monoxide through its oxygen -- which may explain the experimental observations associated with this synthesis and may predict catalyst behavior.

This investigation is designed to test and extend this hypothesis and its many ramifications experimentally, starting with previously studied systems and including various metals and metal oxides not previously studied. In addition, it will develop valuable data on hydrocarbon, olefin, and alcohol syntheses. The identification or synthesis of more efficient catalyst for dilute phase reactions under mild conditions, which would facilitate heat removal, is also considered, as is the possibility of pointing the way to sulfur-tolerant catalysts.

Significant Accomplishments in 1978:

This program was started in FY 1979 and only preliminary studies were started in 1978.

Principal Activities Planned for 1979:

1. Work will concentrate on the carbon-carbon coupling step of the mechanism, a most critical area. Various intermediate species will be prepared and tested for conformity to the proped oxide mechanism.

2. Metal oxide bond strength will be correlated to product distributions. This will be mainly a literature study, but metals with limited information will be experimentally tested.

Publications in 1978:

None.

CYCLIC SEPARATIONS PROCESS RESEARCH

FY 1978: \$140,000

Principal Investigators: F. B. Hill
Y. W. Wong

FY 1979: \$141,000

Sponsor: Basic Energy Sciences (DOE)

Objective:

This program consists of a study of the application of cyclic separation processes to separations problems arising in energy technology. Its objectives are to obtain an understanding of the characteristics and basis of operation of these processes as a class and to explore the feasibility of using them to perform specific separations of interest in the energy field.

Scope:

The cyclic processes of interest include pressure and temperature swing absorption, parametric pumping, cycling zone absorption, and various forms of preparative chromatography. Applications now under study involve isotope separations, specifically tritium removal from nuclear industry effluents and heavy water production. Future work may include applications such as hydrogen purification, pollutant removal from gases, and additional separations problems of interest in nuclear technology.

Elements of the program include development of the theory of cyclic processes, measurement of equilibrium and kinetic properties of fluid-solid separation systems, measurement of the characteristics of single stages of cyclic processes, and process design and evaluation studies.

The work accomplished in this program will permit rational design and assessment of cyclic separation processes and will identify promising methods of solution for specific separation problems in the energy field.

Significant Accomplishments in 1978:

1. A general theory of isothermal heatless adsorption was developed and applied to the case of hydrogen isotope separation on metal hydrides.
2. HT-H₂ separation via heatless adsorption using vanadium hydride was accomplished. The process could be operated to produce a product stream either enriched or depleted in the heavy isotopic species.
3. Experiments were started on a temperature cycling process for hydrogen isotope separation using vanadium hydride.

Principal Activities Planned for 1979:

1. Experimental investigations will be conducted on the temperature cycling process and on the pressure cycling separation, which is apparently based on a kinetic isotope effect.
2. An equilibrium theory of the temperature cycling process will be developed, and a theory for cyclic processes with finite exchange rates will be formulated.
3. Process design and evaluation studies of single and multistage processes for hydrogen isotope separation via cyclic processes using vanadium hydride will be carried out.

Publications in 1978:

Journal Articles

Wong, Y. W. and Hill, F. B. Equilibrium and kinetics studies of hydrogen isotope exchange on vanadium hydride. A.I.Ch.E. Journal (submitted).

Oral Presentations

Wong, Y. W. and Hill, F. B. Separation of hydrogen isotopes via cyclic separation processes: Background study. Presented at A.I.Ch.E. Meeting, Atlanta, Georgia, February, 1978.

Hill, F. B., Wong, Y. W., and Chan, Y. N. Tritium removal using vanadium hydride. Presented at Fifteenth D.O.E. Nuclear Air Cleaning Conference, Boston, Mass., August, 1978.

Hill, F. B., Wong, Y. W., and Chan, Y. N. Equilibrium theory of isotope separation via heatless adsorption. Presented at A.I.Ch.E. 71st Annual Meeting, Miami Beach, Florida, November, 1978.

TRACE ELEMENT ANALYSIS USING SYNCHROTRON RADIATION

FY 1978: ---

Principal Investigators: Barry Gordon
Manny Hillman

FY 1979: \$47,000

Sponsor: Basis Energy Sciences (DOE)

Objective:

The objective of this study is the application of synchrotron radiation x rays to the development of a microprobe for trace element analysis for use in the geological, medical, environmental, and materials sciences.

Scope:

This program is concerned with the application of the National Synchrotron Light Source (NSLS) to multi-elemental trace element analysis. Current analytical techniques, including neutron activation analysis, atomic absorption, and emission spectroscopy, are time consuming and are limited in the numbers of samples and elements that can be analyzed. The sensitivity of energy-dispersive x-ray fluorescence systems has been limited by large backgrounds, delta-ray bremsstrahlung in proton excitation, and coherent and incoherent scattering of the primary beam in photon excitation. This study takes advantage of a synchrotron radiation x-ray source to substantially improve the sensitivity of the x-ray fluorescence technique; multivariate analysis of trace element concentrations provides a means of handling and interpreting the increased amount of data. The NSLS at Brookhaven National Laboratory is one of two in this country capable of providing such an excitation source and is by far the more intense source of x-rays. The rapidity and accuracy of the technique, the simultaneous determination of trace and major elemental concentrations, and the potential for scanning samples with an x-ray microprobe contribute to the usefulness of the technique in performing broad surveys necessary in many fields. Among the more obvious fields of application are geosciences, atmospheric sciences, oceanography, and life sciences.

Significant Accomplishments in 1978:

This is a new program, initiated in October 1978.

Principal Activities Planned for 1979:

1. The investigation of a general system of x-ray spectral analysis for trace element identification and determination will begin. The study will be based on the existing program SAMPO, which has been adapted for x-ray analysis.

2. A study for the design of x-ray detector systems applicable to different modes of trace element analysis will begin.

Publications in 1978:

None.

DETERMINING FRAGILE MOLECULES IN THE ENVIRONMENT

FY 1978: \$110,000

Principal Investigator: R. Tanner

FY 1979: \$110,000

Sponsor: Basic Energy Sciences (DOE)

Objective:

The objective of this study is to devise and develop new analytical methods for the determination of potentially reactive substances in the environment.

Scope:

The long-term goals of this program are to devise and develop fundamentally new analytical methods of high sensitivity and selectivity for the determination of traces of potentially reactive substances in the environment based on derivatization - chromatographic separation - selective detection techniques. Since many substances of interest may be reactive under analysis conditions, derivatization is used to convert the reactive or otherwise fragile substance to a derivative that can be separated from interferents and delivered quantitatively to a detector. Chromatographic techniques (gas, liquid, thin layer, ion exchange) are well-established methods for increasing analytical specificity by separating co-derivatized substances and other interferents from the derivative of interest. Selective detectors, whose response is keyed to a single element or functional group, increase sensitivity by orders of magnitude for substances containing that element or functional group. This reduces the detector response for even gross amounts of potential interferents and simplifies the separation technology. The derivatization - chromatography - selective detection principle is broad and is applicable to analysis of environmental species of dynamically varying concentrations, e.g., nitrate, sulfate, sulfite, organics in aqueous and aerosol samples and ammonia, nitric acid, and others in gaseous samples.

Significant Accomplishments in 1978:

1. Work on a method for nitrate analysis by nitro-derivatization - gas chromatographic separation with electron capture detection (GC-ECD) was essentially completed, and a description was accepted for publication.
2. A method for continuously determining ammonia and primary amines by fluorescent derivatization was developed and prepared for publication.

3. Exploratory work was done on a method to determine S-containing species in solid samples, involving methylation for gas chromatographic separation with flame photometric detection.

4. Background literature work was begun on the characterization of organics (weak acids, bases, condensed hydrocarbons) on solid surfaces by GC-ECD and liquid chromatographic fluorescence techniques.

Principal Activities Planned for 1979:

1. A small amount of effort will be expended on the nitro-derivatization method for nitrate to improve the analytical precision and to assess the suitability of the method for direct analysis of nitrate on inert filter matrices.

2. The fluorescent derivatization method will be studied in detail to elucidate the chemical nature of the derivative and to assess its stability under the conditions of analysis. A continuous analysis scheme involving collection of ammonia in acidic solution in a flow-through impinger will be investigated in detail for feasibility and, if reproducible collection efficiencies for ppb levels of gaseous ammonia can be demonstrated, the system will be implemented.

3. A start will be made on the analysis by derivatization-chromatography for classes of important oxygenated organic compounds in airborne and aqueous particulates, the ion pair extraction and pentafluorobenzyl esterification and GC-ECD analysis of carboxylic and other acidic components of particulate samples, and the class separation and analysis of polynuclear aromatics and their partially oxidized by-products formed in the atmospheric or aqueous environment.

4. Laboratory testing of the method for derivatization of acidic particulate sulfur compounds by methylation with diazomethane followed by GC separation on specially deactivated column materials, and detection with a flame photometric detector, will be completed.

Publications in 1978:

Journal Articles

Tanner, R. L., Fajer, R., and Gaffney, J. Determination of parts-per-billion concentrations of aqueous nitrate by derivatization gas chromatography with electron capture detection. Anal. Chem. (in press); Presented at the Euroanalysis III Conference, Dublin, Ireland, August, 1978.

BNL Reports

Tanner, R. L. and Lepore, J. Continuous determination of ammonia at ambient atmospheric concentrations using fluorescent derivatization. Informal Report BNL 24027.

THE ROTATING FLUIDIZED BED COMBUSTOR

FY 1978: ---

Principal Investigator: F. B. Hill

FY 1979: \$25,000

Sponsor: Basic Energy Sciences (DOE)

Objective:

The objective of this program is to obtain an understanding of the factors influencing the performance of the rotating fluidized bed when used as a chemical reactor and specifically as a reactor for the direct combustion of coal.

Scope:

The rotating fluidized bed is a centrifuge-like device in which fluidizing gas enters a rotating basket radially and causes the fluidization of a bed of particles held against the basket wall by centrifugal force. As a coal combustor, the rotating device should have the following advantages compared with the usual vertical fluidized bed: (1) higher power density, (2) easier startup and turndown, and fewer feed points, and (3) greater stability against elutriation. Disadvantages may include higher pressure drop, greater required heat transfer area, and problems related to the use of rotating equipment.

The present program is designed to make an in-depth engineering research study of the characteristics of this device and to seek ways of exploiting its advantages and overcoming possible disadvantages. The program includes cold bed studies of fluid dynamics topics, hot bed studies of combustion and pollutant generation and retention, and theoretical and modeling studies of multi-g systems. The results will be of value in assessing the general usefulness of the rotating fluidized bed as well as its usefulness as a combustor.

Significant Accomplishments in 1978:

This program was formally initiated in FY 1979. In anticipation of its start, two exploratory investigations were carried out this year:

1. A theoretical study on the motion of bubbles and of entrained particles in the rotating fluidized bed showed that Coriolis deflections of bubbles could be large and that bubble rise was large at low rotational

speeds. The rotating fluidized bed was found to have greater stability against elutriation than the gravitational fluidized bed.

2. A study of the use of a rotating fluidized bed as a filter for dusts and mists indicated that the rotating system may have high filtration efficiency at smaller particle sizes and higher flow rates than the gravitational fluidized bed.

Principal Activities Planned for 1979:

An experimental investigation of the motion of large bubbles in a rotating liquid will be carried out. The results will be compared with the theory developed in the previous year.

Publications in 1978:

None.

HIGH SCHOOL TEACHERS' INSTITUTE ON ENERGY

FY 1978: \$15,000

Principal Investigator: D. J. Metz

FY 1979: \$18,000

Sponsor: National Science Foundation

Objective:

The objectives of this activity are, in general, to intensify and expand the level of interaction between the local secondary school science faculties and the scientific activities and expertise of the Laboratory, and, in particular, to help these high school teachers improve their abilities to teach and to discuss the various facets of our "energy crisis" with their students, colleagues, and communities at large.

Scope:

The Institute is available to teachers of science and mathematics (Grades 9 through 12) in the counties of Nassau and Suffolk, New York. The program consists of thirty evening sessions, each of three hours' duration, during the academic year. The Institute comprises two parallel, complementary activities: (1) lectures delivered by Laboratory staff members, and (2) workshop activities, guided by assigned advisors, who are also Laboratory staff members.

The sessions are divided into three segments, as follows:

Segment I. Discussion of Basic Energy Concepts - 8 sessions

Segment II. In-depth Study of Various Technologies and Conservation Measures - 12 sessions

Segment III. Comparative Analysis of Technologies - 10 sessions

Each participant is required (1) to make an oral presentation, (2) to write a report, and (3) to develop an individual project.

Significant Accomplishments in 1978:

1. The Institute, started in September 1977 under NSF sponsorship, concluded in May 1978, with 30 participants (of an original enrollment of about 40) completing all the requirements.

2. The program was offered again under NSF sponsorship starting in September 1978. The initial enrollment was approximately 37, and had decreased to 28 by the end of the calendar year.

Principal Activities Planned for 1979:

1. The Institute started in September 1978 will end in May 1979, with 28 participants expected to fulfill all the requirements.

2. If the program is funded again by NSF, another offering of the Institute will be made, starting in September 1979.

Publications in 1978:

None.

PROGRAMS PROPOSED FOR INITIATION IN FY 1980

In addition to the programs summarized above, the Chemical Sciences Division has proposed to undertake a new program in FY 1980: Specific Molecular Property Detectors for Chromatographic Analysis.

METALLURGY AND MATERIALS SCIENCE DIVISION

Masaki Suenaga

The Metallurgy and Materials Science Division performs basic and applied research on the characterization of material properties and behavior under a variety of conditions; its activities also include the development of materials for applications in advanced energy systems, and support to other programs within the Department of Energy and Environment and elsewhere at the Laboratory.

~~1874~~ Currently a major effort of this Division is the investigation of superconducting properties of Al₅ compounds with high critical-temperature, of high critical-temperature and critical-current superconductors, and the relationship of these properties to fabrication techniques, metallurgical treatments, nonhydrostatic stresses, and irradiation with protons, neutrons, and electrons. The applications of these materials to power transmission cables and high-field magnets are studied. New programs have been started to investigate materials problems in other energy-related technologies, such as metallurgical problems in metal hydrides, high temperature fracture failures and hydrogen embrittlement of structural materials, and development of amorphous semiconductors for solar energy applications. New techniques such as energy-dispersive x-ray compositional analysis with a transmission electron microscope, small-angle neutron scattering, and extended x-ray absorption fine structure studied with synchrotron radiation will be employed as programs require them.

RELATIONSHIP BETWEEN PROPERTIES AND STRUCTURES

FY 1978: \$620,000

Principal Investigators: D. Dew-Hughes,
O. Kammerer, C. Pande, M. Suenaga,
D. O. Welch

FY 1979: \$570,000

Sponsor: Basic Energy Sciences (DOE)

Objective:

The objective of this program is to perform basic studies on the relationship of defects to the macroscopic properties of superconducting materials and to provide the basic data and understanding of the fundamental physical metallurgy of superconducting materials required for their effective practical utilization.

Scope:

The task of this program is to study the basic relationship between microscopic structure and macroscopic properties, with emphasis on superconducting materials with high critical-temperatures and high critical-magnetic fields. Superconducting compounds with the A15 crystal structure, such as Nb_3Sn , V_3Ga , etc., are of primary interest, but compounds with other structures, such as Laves and Chevrel phases, are also included. The research is focussed on the basic physical properties of superconducting compounds and on the nature and behavior of lattice defects, especially their role in altering superconducting properties such as critical temperature, magnetic field, and current density. Also under investigation are techniques for producing new superconducting materials, ranging from explosive formation of Nb_3Si to methods for producing multifilamentary conductors utilizing compounds with high critical temperature and magnetic field other than Nb_3Sn and V_3Ga .

Significant Accomplishments in 1978:

1. A superconducting A15 niobium-silicon (Nb_3Si) was formed by explosive compression of the Nb_3Si tetragonal phase.
2. Young's modulus of polycrystalline Nb_3Sn was measured between 4.2 and 300 K by static beam-deflection methods. It was found to be proportional to $\ln T$ between 50 and 300 K and to be temperature independent below the superconducting critical temperature, 18 K.
3. Superconducting niobium-tin (Nb_3Sn) wires, made by the "bronze" process using Nb-Ta alloy cores, were found to exhibit very high critical current densities (twice as high as that of unalloyed Nb_3Sn) at 16 tesla.

Principal Activities Planned for 1979:

1. Improved fabrication methods for multifilamentary Nb₃Sn wires will be investigated.
2. The properties of simple point defects and the effects of disorder and deviations from stoichiometry on the lattice parameter of Nb₃Sn will be calculated by using a theory in which the interatomic forces are derived from "high temperature" properties of Nb₃Sn.
3. Effects of uniaxial stress on superconducting transition temperatures of Al₅ superconductors will be investigated.

Publications in 1978:

Journal Articles:

Bussiere, J. F., Onishi, T., Welch, D. O., and Suenaga, M. Stress-induced enhancement of T_c in bronze-processed V₃Ge. Appl. Phys. Lett. 32, pp. 686-688 (1978).

Caton, R. and Sweedler, A. R. The dependence of the superconducting transition temperature on silicon concentration in the NbAlSi ternary system. J. Less-Common Met. 60, pp. 91-100 (1978).

Caton, R. and Viswanathan, R. Normal state resistivity of single crystalline V₃Si as a function of neutron irradiation. J. de Phys. 39, C-6, pp. 385-386 (1978).

Dew-Hughes, D. Solid state (bronze process) V₃Ga from V-Al alloy core. J. Appl. Phys. 49, pp. 327-332 (1978).

Dew-Hughes, D., Moehlecke, S., and Welch, D. O. Recovery by annealing of irradiated Al₅ compounds. J. Nuclear Materials, 72, pp. 225-232 (1978).

Dew-Hughes, D. and Suenaga, M. Critical current densities of bronze-processed Nb₃(Sn_{1-x}Ga_x) wires up to 23.5 tesla. J. Appl. Phys. 49, pp. 936-938 (1978).

Luhman, T. S. and Dew-Hughes, D. Superconducting wires of PbMo_{5.1}S₆ by a powder technique. J. Appl. Phys. 49, pp. 936-938 (1978).

Pande, C. S. A mechanism for the degradation of superconducting transition temperatures on high energy neutron irradiation in Al₅ compounds. J. Nuclear Materials 72, pp. 83-87 (1978).

Pande, C. S. and Viswanathan, R. Comment on the paper "EXAFS measurements on Nb₃Ge thin films" by G. S. Brown et al. Solid State Commun. 26, pp. 893-895 (1978).

Pande, C. S. and Viswanathan, R. Scattering of x-rays in irradiated Al₅ compounds. J. Less-Common Met. 62, pp. 119-126 (1978).

Pande, C. S. and Viswanathan, R. The nature of the defects in neutron irradiated Al₅ compounds. J. de Phys. 39, C-6, pp. 389-390 (1978).

Pande, C. S. and Viswanathan, R. A possible mechanism for T_c degradation in as-grown Nb₃Ge films. Presented at the 1978 March meeting of the American Physical Society, Washington, D.C., March, 1978; Bull. Am. Phys. Soc. 23, p. 384 (1978).

Richter, D. S. and Welch, D. O. A theoretical estimate of the strain-dependent elastic dipole tensor for interstitial impurities in b.c.c. metals and of the strength of the non-linear Snoek effect. Scripta Met. 12, pp. 831-835 (1978).

Suenaga, M., Onishi, T., Welch, D. O., and Luhman, T. S. Influence of stress on the superconducting properties of "bronze processed" Nb₃Sn wires. Presented at the 1978 March meeting of the American Physical Society, Washington, D.C., March 1978; Bull. Am. Phys. Soc. 23, p. 229 (1978).

Sweedler, A. R., Cox, D. E., and Moehlecke, S. Neutron irradiation of superconducting compounds. J. Nuclear Materials 72, pp. 50-69 (1978).

Varmazis, C., Viswanathan, R., and Caton, R. A technique for bonding Au and Ag metals on sapphire. Rev. Sci. Instrum. 49, pp. 549-550 (1978).

Viswanathan, R. and Caton, R. Effect of neutron irradiation on single crystal V₃Si: heat capacity and resistivity. Phys. Rev. B 18, pp. 15-21 (1978).

Viswanathan, R., Caton, R., and Pande, C. S. Superconducting transition-temperature widths in neutron-irradiated single crystal V₃Si. Phys. Rev. Letters 41, pp. 906-910 (1978).

Viswanathan, R., Caton, R., and Pande, C. S. Superconductivity in irradiated Al₅ compounds at low fluences. I. Neutron-irradiated V₃Si. J. Low Temp. Phys. 30, pp. 503-511 (1978).

Welch, D. O. and Richter, D. S. Model calculations of the strain-dependent elastic dipole tensor for interstitial impurities in b.c.c. metals. Presented at the 1978 March meeting of the American Physical Society, Washington, D.C., March 1978; Bull. Am. Phys. Soc. 23, p. 257 (1978).

Welch, D. O. and Lynn, K. G. An approximate method for calculating the lifetime of positrons trapped by lattice defects. J. Nuclear Materials 69-70, pp. 611-612 (1978).

Welch, D. O. Lazareth, O. W., Dienes, G. J., and Hatcher, R. D. Clusters of alkali halide molecules. J. Chem. Phys. 68, pp. 2159-2171 (1978).

Welch, D. O., Paskin, A., and Dienes, G. J. A molecular dynamical study of the equation of state of solids at high temperature and pressure. J. Phys. Chem. Solids 39, pp. 589-603 (1978).

Dew-Hughes, D. and Luhman, T. S. The thermodynamics of Al₅ compound formation by diffusion from ternary bronzes. J. Material Sciences 13, pp. 1868-1876 (1978)

Dew-Hughes, D. Phase diagram information for processing of superconductors. Applications of Phase Diagrams in Metallurgy and Ceramics, NBS Special Publication #496, pp. 1411-1417 (1978): Phase Diagrams NBS, Gaithersburg, MD, Jan. 10-12, 1977.

Oral Presentations:

Welch, D. O. Current status of theoretical research in the area of high-temperature ceramics. DOE High-Temperature Ceramics Panel Meeting, Snowbird, UT, July 6-11, 1978.

RADIATION DAMAGE

FY 1978: \$200,000

Principal Investigator: C. L. Snead, Jr.

FY 1979: \$210,000

Sponsor: Basic Energy Sciences (DOE)

Objective:

The objective of this study is to develop an understanding of the physical mechanisms that relate radiation-induced lattice defects in type-II superconductors to the superconducting critical properties, and to apply positron-annihilation techniques to the study of defects.

Scope:

The purpose of this program is twofold: (1) to investigate property changes in materials that result from energetic-particle radiation damage, and (2) to utilize the observed property changes to obtain information on the nature of the damage caused by different types of irradiation. Emphasis is on the first type of investigation, in which the critical properties of type-II superconductors are studied as a function of several types of irradiation damage. This provides information on the response to be expected when high-field magnets are operated in radiation environments, e.g., ISABELLE and fusion-reactor magnets. Various radiation-damage sources are used to provide controlled sources of defects in superconductors so that the physical mechanisms coupling defects to changes in critical properties can be elucidated. Such information is useful also for the second type of study, in which comparison of property changes due to different types of particle damage can help elucidate the nature of the damage created by each. Determinations of the defect state in mainly high-energy-proton and neutron-irradiated specimens are achieved by relating the above critical-property measurements to measurements of other properties such as microhardness and electron microscopy, and to damage-energy analyses. Still other measurements, e.g., of positron annihilation and dynamic Young's modulus, are also used to determine the effect of defects on the properties of superconductors and other materials of importance in advanced energy-production devices.

Significant Accomplishments in 1978:

1. Determination of the neutron radiation response of the critical current as a function of field of $\text{Nb}_3(\text{SnGa})$ up to H_{c2} was accomplished with the finding of limiting behavior of H_{c2} in specimens of highest T_c and normal-state resistivity.

2. By using positron lifetime and Doppler-broadening measurements, the swelling curve was determined for neutron-irradiated Mo and Mo-1/2-at.% Ti. A peak at $\sim 600^{\circ}\text{C}$ was defined and a skewness of the peak to high temperatures (1500°C) was observed.

Principal Activities Planned for 1979:

1. 4.2 K electron-damage studies will be performed on Al₅ thin films with anneals from 4.2 to room temperature.

2. Positron studies of HFBR neutron-irradiated Si and Ge single crystals and high-energy-neutron irradiated metals will open up new aspects of investigating defects.

Publications in 1978:

Journal Articles:

Snead, C. L., Jr. Low-temperature 30-GeV-proton effects on critical properties of type-II superconducting filamentary conductors. J. of Nuc. Materials 72, 190 (1978).

Ghosh, A. K., Wiesmann, H., Gurvitch, M., Lutz, H., Kammerer, O. F., Snead, C. L., Jr., Goland, A., and Strongin, M. The effects of irradiation at cryogenic temperatures and electron irradiation at cryogenic temperatures and electron irradiation on T_c and the transport properties of Al₅ superconductors. J. of Nuc. Materials 72, 70 (1978).

Gurvitch, M., Ghosh, A. K., Snead, C. L. Jr., and Strongin, M. Measurements of gap anisotropy in Al₅ Nb₃Sn. Phys. Rev. Letts. 39, 1102 (1977).

Snead, C. L., Jr. and Suenaga, M. Neutron-irradiation effects in the pseudo-binary compound Nb₃(SnGa): changes in T_c , I_c , and flux pinning. Proc. of the Applied Superconductivity Conf., Pittsburgh, PA, Sept. 25-28, 1978 (submitted).

Snead, C. L., Jr. Polymer utilization in transmission line application. Proc. of the Polymer Materials Basic Research Needs for Energy Applications Workshop, CONF 780643, 1978, p. 67 (submitted).

Oral Presentations:

Snead, C. L., Jr., Lynn, K. G., Goland, A. N., and Wiffen, F. W. Swelling of neutron-irradiated Mo and Mo-1.5 Ti by means of positron annihilation. Presented at the March Meeting of the American Physical Society, Washington, D.C., March 1978.

FABRICATION AND PROPERTIES OF CONDUCTORS FOR MFE MAGNETS

FY 1978: \$200,000

Principal Investigators: T. S. Luhman,
M. Suenaga, W. B. Sampson

FY 1979: \$200,000

Sponsor: Magnetic Fusion Energy (DOE)

Objective:

The objective of this program is to develop suitable and economical conductors for mirror and tokamak fusion reactor magnets.

Scope:

This program is concerned with the mechanical and metallurgical aspects of designing, fabricating, and utilizing superconducting composite conductors in fusion magnet systems. Particular emphasis is on understanding and improving the mechanical and high-field superconducting properties of Al5 diffusion-processed conductors. Experimental determinations of superconducting properties are the basis of the technical approach. Experiments focus on factors that affect application. These include experimental determination of superconducting critical currents, temperatures, and magnetic fields under tensile and bending strains, and metallurgical investigations designed to improve high-magnetic-field superconducting critical currents. Experimental test facilities have been built for in situ work at 4.2 K and 4.0 and 8.0 tesla. Primary conductors of interest thus far have been monofilament Nb₃Sn wires, multifilamentary Nb₃Sn wires, and multifilamentary cabled Nb₃Sn conductors.

An accurate assessment of mechanical and high-field superconducting properties under strain is necessary to facilitate the use of Al5 conductors in large magnet systems. Once this is available, winding and operational design limits can be set. Selection of filament size and spacing, the ratio of the matrix to the filaments, and the alloy content of the superconducting compound can be used to design conductors for specific uses.

Significant Accomplishments in 1978:

1. A thorough understanding of the relationship between changes in T_c , H_{c2} , and $J_c(H)$ and the ratio of the matrix (Cu-Sn alloy) to the core (Nb and Nb₃Sn) was achieved.
2. Mechanical properties of Nb₃Sn wires made by the "bronze" process were improved significantly by the addition of ~0.2% Be to the Cu-Sn matrix.

Principal Activities Planned for 1979:

1. Effects on critical currents of strains due to bending of Nb_3Sn wires will be clarified.
2. Mechanical properties of mono- and multifilamentary Nb_3Sn wires will be compared.

Publications in 1978:

Journal Articles:

Luhman, T., Suenaga, M., and Klamut, C. J. Influence of tensile stresses on the superconducting temperature of monofilamentary Nb_3Sn composite conductors. *Advances in Cryogenic Engineering*, 24, pp. 325-330 (1978).

Luhman, T., Suenaga, M., Welch, D. O., and Kaiho, K. Degradation mechanisms of Nb_3Sn composite wires under tensile strain at 4.2 K. *Applied Superconductivity Conference*, Pittsburgh, PA, September 25-28, 1978: *IEEE Trans. on Magnetics*, MAG-15, pp. 669-702 (1979).

Suenaga, M., Onishi, T., Welch, D. O., and Luhman, T. S. Influence of stress on the superconducting properties of "Bronze Processed" Nb_3Sn wires. Presented at the Washington, D.C. Meeting of the American Physical Society, March 27-30, 1978: *Bull Am. Phys. Soc.* 23, pp. 229 (1978).

Luhman, T. Increases in the allowable strain limits for Nb_3Sn wire conductors by alloying the bronze matrix with Be. *Applied Physics Letters*, July 1978 (submitted).

Suenaga, M., Luhman, T. S., Sampson, W. B., Onishi, T., and Klamut, C. J. Fabrication and properties of conductors for fusion magnets. *Workshop on Development of Superconductors for Fusion Power*, Germantown, MD, January 26, 1978. To be published in DOE Report.

SUPERCONDUCTING POWER TRANSMISSION LINES*

FY 1978: ~\$400,000

Principal Investigators: J. F. Bussiere,
C. Klamut, A. Muller, M. Suenaga

FY 1979: ~\$400,000

Sponsor: Electric Energy Systems (DOE)

Objective:

The objective of this program is to develop superconducting and dielectric tapes for ac superconducting power transmission lines.

Scope:

The work on superconducting tapes includes investigation of fabrication processes for tapes suitable for ac (60-Hz) applications, of mechanisms for ac losses in Al₅ compounds, of relationships between microstructures and losses, and of mechanical properties of the tapes. In addition, new processes for conductor fabrication will be transferred to industry, and the contracts for commercialization of the processes will be monitored.

The work on dielectric tapes is centered on investigation of dielectric materials to provide tapes that are electrically, mechanically, and thermally suitable for use as insulation on ac superconducting cables. Also, a radiographic technique for studying tape-lapping patterns and locating mechanical defects in existing cables is being developed and applied. Measurements of mechanical (strength, friction, etc.) and thermal (expansion coefficients) properties of these tapes are made at room as well as liquid helium temperatures.

Significant Accomplishments in 1978:

1. A large bronze billet containing a rectangular Nb-1% Zr core was successfully extruded and cold-rolled to produce a very high yield of Nb₃Sn tape.
2. The mechanical strength was increased and the dielectric loss was reduced for the three-ply laminate polypropylene dielectric film under development for the superconducting power transmission cable.
3. New radiographic techniques were used at the Westinghouse Cable Test Facility at Waltz Mill, PA, to show the extent of damage in cables that had experienced severe thermo-mechanical bending.

*This represents an effort by the Division of Metallurgy and Materials Science for the program by the same title in the Accelerator Department.

4. The temperature dependence of Young's modulus for Nb₃Sn was measured between 300 and 4 K.

Principal Activities Planned for 1979:

1. The superconducting tape for the 100-meter test line will be received, evaluated, and wound into the test cable.
2. Development of very high modulus polyolefin tapes will continue.
3. Studies of the compatibility relationship between polyolefin films and hot hydrocarbon oils will be initiated.

Publications in 1978:

Journal Articles:

Bussiere, J., Onishi, T., Welch, D. O., and Suenaga, M. Stress-induced enhancement of T_c of bronze-processed V₃Ge. Appl. Phys. Lett. 32, p. 686 (1978).

Bussiere, J. and Kovachev, V. T. Surface effects affecting ac losses of Nb₃Sn. J. Appl. Phys. 49, p. 2526 (1978).

Bussiere, J. and Clem, J. Effect of trapped magnetic flux on ac losses of Nb₃Sn. IEEE Transactions on Magnetics, MAG-15, p. 264 (1979).

Bussiere, J., Kovachev, V., Klamut, C., and Suenaga, M. Nb₃Sn conductors for ac power transmission: electrical and mechanical characteristics. Adv. Cryo. Eng., Vol. 24, pp. 449-458 (1978).

Bussiere, J. and Kovachev, V. T. ac losses of bronze-processed (Nb_{1-x}Zr_x)₃Sn between 5 and 16 K. J. Appl. Phys. (submitted).

Muller, A. C. Properties of plastic tapes for cryogenic power cable insulation. Presented at the 1978 ICMC Meeting, Munich, Germany, July 10-11, 1978 (submitted).

Muller, A. C. X-ray examination of taping structure in lapped high voltage underground power transmission cable. 1979 Fall ASNT Meeting, St. Louis, MO, October 1979 (submitted).

Muller, A. C. Polymeric films for use on superconducting power transmission cables. Presented at the American Institute of Chemical Engineers 71st Annual Meeting, Miami, Florida, November 12-16, 1978 (submitted).

Muller, A. C., McNerney, A. J., Thomas, R. A., Pearmain, A. J., and Kosaki, M. Lapped insulation for a superconducting power transmission line, Presented at the 5th Symposium on Superconducting Power Transmission, Brookhaven National Laboratory, October 5-6, 1978.

PHYSICAL METALLURGY OF METAL HYDRIDE SYSTEMS

FY 1978: \$100,000

Principal Investigators: M. Pick,
D. O. Welch, D. Dew-Hughes, C. Pande

FY 1979: \$150,000

Sponsor: Basic Energy Sciences (DOE)

Objective:

The objective of this study is to gain a fundamental understanding of the metallurgical factors influencing the hydriding behavior of certain metals and alloys.

Scope:

Of particular interest in achieving this objective are the effects of microstructure, lattice defects, alloying, and surface properties on the thermodynamics, kinetics, and mechanisms of hydrogen uptake and release in transition metals, solid solutions, and intermetallic compounds. The effect of dissolved hydrogen on fracture strength is also of interest. The research includes study of the thermodynamics of equilibrium phase relationships in selected transition metal solid solutions; study of the kinetics of hydrogen uptake and release, and the role of surface condition therein, for various transition metals; measurement of the fracture characteristics of transition metals containing hydrogen; and structural and microstructural studies using optical, x-ray diffraction and absorption, and electron microscopic techniques. The results of this research should be of value in the development of metal hydrides for use as energy storage media and should contribute to the basic understanding of interstitial solid solutions in metals.

Significant Accomplishments in 1978:

1. An activation barrier to hydrogen solution in Ta and Nb was observed as well as the existence of strong surface traps.
2. Transmission electron microscopy of iron-titanium hydride showed that the hydride at low hydrogen level forms as partially coherent plates and grows in the form of narrow, adjacent domains with different orientations.
3. Equilibrium pressure-composition-temperature relations were measured for pure niobium and for niobium containing small additions of vanadium, and a theoretical model of the effects of hydrogen trapping on phase equilibria in the α - α' region of such systems was constructed.

Principal Activities Planned for 1979:

1. The kinetics of hydrogen uptake and release from Nb and Ta surfaces cleaned in ultrahigh vacuum will be investigated.
2. Hydrogen trapping by solute atoms in dilute solid solutions will be studied by EXAFS measurements of changes in the substitutional solute-atom environment upon hydriding.

Publications in 1978:

Journal Articles:

Thompson, P., Pick, M. A., Reidinger, F., Corliss, L. M., Hastings, J. M., and Rielly, J. J. Neutron diffraction study of β -iron titanium deuteride. J. Phys. F8, pp. L75-80 (1978).

Lee, K. S. and Dew-Hughes, D. The effect of hydrogen on the mechanical properties of Fe whiskers. Presented at the 1978 Fall Meeting of the Metallurgical Society of AIME, St. Louis, MO, October 15-19, 1978 (submitted).

EFFECTS OF MICROSTRUCTURE AND ENVIRONMENT UPON FRACTURE TOUGHNESS

FY 1978: \$100,000

Principal Investigators: A. Arbel,
S. Hwang

FY 1979: \$180,000

Sponsor: Basic Energy Sciences (DOE)

Objective:

The objective of this program is to study the relationship between microstructure and fracture toughness in metals and alloys.

Scope:

The purpose of this research is to make a fundamental study of the relationship between the microstructures of materials and their fracture toughness (a property characterizing the resistance of a material to the propagation of cracks in it) and to contribute to the advancement of a method of extracting useful information about fracture toughness from small specimens. The study is done by developing particular well-characterized microstructures in commercially pure metals, solid solutions, and precipitation-hardened superalloys either by high-temperature monotonic and cyclic creep or by fully reversed low-cycle strain-controlled loading, and subsequently measuring the fracture toughness. This study will yield information on the fundamental nature of fracture in materials of practical interest while at the same time contributing to the development of methods of selection and evaluation of structural materials for use in energy-generating applications.

Significant Accomplishments in 1978:

1. The effect of monotonic creep on the fracture toughness of as-received Hastelloy C-4 was studied for loading in the temperature range 600°-750°C at various stress levels.

Principal Activities Planned for 1979:

1. Efforts will be continued to establish the effect of monotonic creep on the fracture toughness of annealed Hastelloy C-4 and of a commercially available precipitation-hardenable alloy, Inconel X-750.

2. Work will be initiated on the effect of fracture toughness of cyclic reverse straining at high temperatures.

Publications in 1978:

Journal Articles:

Arbel, A. and Warren, J. The effect of creep on the fracture of metals. Presented at the 1978 Fall Meeting of the Metallurgical Society of AIME, St. Louis, MO, October 15-18, 1978 (submitted).

INTERGRANULAR STRESS CORROSION OF IRON AND NICKEL BASE ALLOYS*

FY 1978: \$60,000

Principal Investigator: A. Winter,
C. Pande

FY 1979: \$60,000

Sponsor: Basic Energy Sciences (DOE)

Objective:

The objective of this study is an understanding of the influence of grain boundary precipitates on intergranular stress corrosion (ISC) of iron and nickel base alloys.

Scope:

ISC in Fe and Ni alloys is a universal problem in the use of these alloys in energy conversion. It has occurred widely in both fossil- and nuclear-fueled power plants and can be anticipated to occur in advanced reactors and in solar or geothermal power generators. The phenomenon is of concern in the performance of steam generators, steam-driven turbine components, and steam lines, which are common to all types of energy conversion systems using a steam cycle. ISC arises from an electrochemical cell being set up in a given environment, at the grain boundary of the alloy. This, for reasons that are not well understood, causes continued corrosion of the grain boundary material. The stress causes local depassivation of the material by rupturing the passivating oxide films and retards repassivation. There is thought to be direct competition between the electrochemical dissolution along the grain boundary and the repassivation reactions. Clarification of this competition could lead to improving the performance of materials by modifying their composition and environment. The most important environments to investigate are those that either are oxidizing or contain dissolved caustics.

Significant Accomplishments in 1978:

1. A method was developed for controlling the contamination rate on a specimen examined in a transmission electron microscope for chemical analysis.

Principal Activities Planned for 1979:

1. Depleted zones adjacent to grain boundaries in stainless steels, Inconel, and incoloy will be studied.

*This represents an effort by the Division of Metallurgy and Materials Science for the program by the same title in the Department of Nuclear Energy.

BASIC PROCESSES AND MICROSTRUCTURAL PROPERTIES
OF AMORPHOUS SEMICONDUCTORS

FY 1978: \$ 60,000

Principal Investigator: R. W. Griffith

FY 1979: \$150,000

Sponsor: Basic Energy Sciences (DOE)

Objective:

The objective of this program is to advance the basic understanding of the physical, chemical, and microstructural properties of passivated amorphous semiconductor materials, with special emphasis on the nature of chemical bonding and the role of localized gap states.

Scope:

Fundamental investigations will be carried out on new passivated amorphous semiconductor (a-SC) materials in order to advance the basic understanding of optoelectronic processes and microstructural manifestations of this genre. The research can provide a foundation for insight into limiting processes in solar energy conversion such as (1) minority-carrier transport in amorphous photovoltaic devices, and (2) optical behavior of a-SC materials at elevated temperature, which may be relevant to solar thermal conversion. The amorphous materials to be synthesized and characterized include doped and undoped valence IV, III, and III-V semiconductor alloys in which, e.g., recombination-center passivation is achieved by hydrogenation and/or halogenation. In order to optimize the optoelectronic quality of passivated a-SC materials, at least two general classes of phenomena will be correlated as functions of processing in plasma deposition. (1) Basic plasma kinetics and surface reactions that involve radical species will be studied by optical-emission and molecular-absorption spectroscopy and by mass-spectrometric techniques. (2) For as-deposited films, the nature of localized gap states and chemical bonding, and the associated role of the electron-phonon interaction, will be studied in the context of fundamental optical, transport, and microstructural properties; techniques will include vibrational spectroscopy, optoelectronic measurements of photoluminescence and photoconductivity, and electron microscopy. In addition, upon completion of the unique National Synchrotron Light Source facility, a twofold effort will be undertaken that greatly complements the preceding approach. Namely, studies will be initiated on electronic states with photoemission spectroscopy and on structural properties at semiconductor surfaces (and interfaces) with EXAFS techniques.

Significant Accomplishments in 1978:

1. The basic capacitively-coupled rf glow-discharge plasma deposition system was completed in our laboratory; this is a reactor designed for reproducible film growth and incorporating a variety of processing features.

2. Experimental apparatus was set up for optical emission spectroscopy studies and for the initial optoelectronic experiments on photoconductivity measurement.

Principal Activities Planned for 1979:

1. Spectroscopy studies will be carried out to identify free radical species in plasma deposition of thin films.

2. Basic optical, transport, and microstructural properties will be investigated for as-deposited passivated a-SC materials such as a-Si:H alloys and more novel materials. For example, photoconductivity measurements at low temperatures can probe basic "hopping" mechanisms; vibrational spectroscopy can decipher bonding patterns in films; and electron microscopy studies using transmission diffraction methods can probe defect systems that may be correlated with electrical behavior.

Publications in 1978:

Journal Articles:

Griffith, R. W. Fundamental aspects of amorphous semiconductors in solar thermal conversion. Proc. Seventh Intern. Conf. Amorphous and Liquid Semiconductors, Edinburgh, July, 1977, W. E. Spear, Editor, pp. 457-461, G. G. Stevenson Ltd., Dundee, 1977.

Griffith, R. W. Amorphous semiconductors in photovoltaic and solar thermal conversion. Proc. Intern. Solar Energy Congress, New Delhi, Jan. 1978, Pergamon, New York, 1978 (in press).

ADVANCED AMORPHOUS MATERIALS FOR PHOTOVOLTAIC CONVERSION

FY 1978: ---

Principal Investigator: R. W. Griffith

FY 1979: \$200,000

Sponsor: Solar Technology (DOE)

Objective:

The purpose of this program is to investigate passivated amorphous semiconductor materials in order to achieve higher photovoltaic conversion efficiencies in low-cost solar cells that are fashioned using such novel materials.

Scope:

Potentially cost-effective solar cells may be fabricated using amorphous semiconductor thin films deposited by the glow-discharge technique. However, for proof of commercial feasibility, it is essential to attain reasonable photovoltaic conversion efficiencies (~10%) in reproducible large-area solar cells. For the particular case of hydrogenated amorphous silicon alloys (a-Si:H), fairly long recombination lifetimes have been found for majority-carrier electrons. Nonetheless, minority-carrier transport so far limits the performance of devices that are fashioned using both doped and undoped films of a-Si:H. For example, in n-type-semiconductor metal-insulator-semiconductor (MIS) Schottky barriers, marginal hole transport is responsible for small values of the short-circuit current density, J_{sc} . Therefore, new amorphous semiconductor materials, in which recombination centers are passivated, will be investigated by advanced plasma deposition techniques. The objective is to improve minority-carrier transport (and the fill-factor) and ultimately raise conversion efficiencies of devices. A partial survey of such alloys includes valence IV, III, and III-V amorphous semiconductors passivated by hydrogenation and/or halogenation. For economic viability, all materials selected must have a sizable resource base, as exemplified by the special case of the alloy a-Si:F:H. A dual determination of key transport parameters will be made for as-prepared films: these include the majority-carrier lifetime and the minority-carrier diffusion length. For the most promising materials that emerge from the initial optoelectronic characterization, devices such as MIS structures will be fabricated, and their conversion efficiencies will be determined. Finally, exploratory studies will be initiated that involve laser recrystallization of amorphous layers. Ultra-thin junctions with high carrier lifetimes near cell surfaces could result from such research.

Principal Activities Planned for 1979:

1. Alloys of a-Si:H that serve as film standards will be grown by plasma deposition and characterized for optoelectronic quality.
2. Additional passivated amorphous semiconductors will be investigated for their suitability in photovoltaic conversion.
3. Prototype devices will be fabricated, and illuminated I-V curves will be obtained.

Publications in 1978:

Journal Articles:

Griffith, R. W. Fundamental aspects of amorphous semiconductors in solar thermal conversion. Proc. Seventh Intern. Conf. Amorphous and Liquid Semiconductors, Edinburgh, July, 1977, W. E. Spear, Editor, pp. 457-461, G. G. Stevenson Ltd., Dundee, 1977.

PITTING RESISTANT MATERIALS FOR GEOTHERMAL APPLICATIONS

FY 1978: --

Principal Investigator: D. van Rooyen

FY 1979: \$150,000

Sponsor: Division of Geothermal
Energy (DOE)

Objective:

This program is intended to develop new iron-base alloys in the Cr-Mn-Mo-N-Ni group with lower cost but with pitting resistance equal to that of more expensive N-free alloys. A secondary task is to examine the mechanism of pitting corrosion. The funding of the program includes a requirement that BNL monitor technical aspects of subcontract work for DOE.

Scope:

Geothermal components, both above ground and in the well, must be made resistant to highly corrosive environments for prolonged periods in order to ensure cost-effective energy conversion. An experimental program has been undertaken to examine compositional factors as part of an applied as well as basic research investigation into the behavior of stainless alloys. The major part of the program deals with effects of alloying additions on the pitting corrosion of stainless alloys containing Fe-Cr-Mn and reduced Ni. Emphasis is on Mo, Cr, and N, because they are the alloying additions most effective for improving resistance to pitting and corrosion in Fe and Ni-base alloys. N is included because Type 216 has better pitting resistance than 316 stainless steel, and it would be useful to find out whether N can improve the properties of other alloys also. Success of this approach would allow reduction of the content of the expensive constituents (Mo, Ni, Cr) in a whole spectrum of alloys by substituting Mn and N. A minor part of the program is exploration of the mechanism of the corrosion process involved in order to improve the basis for producing better alloys for use in geothermal energy systems. The literature indicates that, the more corrosion resistant an alloy, the better its passive film. However, an active pit is thought to remain active because it is covered by a thin membrane of oxide, which traps a highly corrosive electrolyte underneath, permitting pitting to proceed. Disruption of this oxide causes pits to lose their activity through loss of the highly corrosive local electrolyte. The ways composition can be used to manipulate oxide film properties to retain passivity but avoid pitting needs to be clarified.

Accomplishments in FY 1978:

The new program of in-house research at BNL was started in FY 1979, supplemented by technical supervision of subcontracts in related fields. Only the BNL R&D effort is discussed below.

Principal Activities for 1979:

The electronic apparatus and necessary laboratory space for measuring the basic parameters of pitting corrosion have been acquired and set up. A titanium autoclave system is expected to be operative by fall of 1979. Equipment for preparing and processing small heats of special alloy compositions is already available, and a beginning has been made in the production of small heats of experimental alloys. During 1979, considerable progress is anticipated in experiments that will define the role of alloy composition. Experiments will be done to distinguish the initiation from the propagation stages of pitting, and to relate these to the nature of the corrosive medium and the surface oxide film on alloys of various compositions.

A review of R&D requirements will be prepared for DOE subcontract work. The first of the additional programs will involve improving the hot fracture toughness and hardness of materials for brine pump bearings and drill bit components, with a stipulation that corrosion resistance be retained. Other material requirements are being reviewed, and additional technical requirements for request for proposals (RFP's) will be summarized.

Publications in 1978:

None - new program.

PROCESS SCIENCES DIVISION

Meyer Steinberg

The Process Sciences Division is concerned with the application of scientific and engineering principles for the development of processes dealing with energy production and conversion. Current programs include the areas of fuel production, conservation, environmental, and related materials problems.

Included under energy and fuel production are the development of advanced coal hydrogenation processes for liquid and gaseous hydrocarbon fuels, the development of improved materials of construction for use in geothermal electrical generation and process and district heating applications, and the development of high-temperature cementing materials for use in the completion of geothermal and deep oil wells.

Energy conservation programs include an advanced process for the production and characterization of energy conservative copolymers for the plastics market and the use of recycled solid wastes as substitutes for energy-intensive materials of construction.

Environmentally oriented programs in progress include methods for the regeneration of limestone used in coal desulfurization processes for application to fluidized-bed combustion and analysis of control technology problems related to coal conversion and global CO₂ emissions.

Structurally, the Division is divided into three units: a Geothermal and Materials Systems Group, a Fossil Energy Sciences Group, and a Process Analysis and Advanced Energy Systems Section.

Concrete-polymer materials are also being developed as improved materials of construction for highway applications.

ALTERNATE MATERIALS OF CONSTRUCTION
FOR GEOTHERMAL APPLICATIONS

FY 1978: \$220,000
FY 1979: \$400,000

Principal Investigator: L.E. Kukacka
Sponsor: Geothermal Energy (DOE)

Objective:

The objective of the program is to develop low-cost nonmetallic materials such as polymers, concrete-polymer composites, and refractory cements for use as materials of construction in geothermal processes.

Scope:

A serious problem in the development of geothermal energy is the limited availability of durable and economic materials of construction for handling hot brine and steam. Hot brine and other aerated geothermal fluids are highly corrosive and chemically attack most conventional materials of construction. Corrosion and scaling have been encountered in all geothermal plants, and, to various degrees, they adversely affect plant lifetimes and power output. To date carbon steel has been the primary material used, but expensive materials such as stainless steels and titanium base alloys may be required for long-term operation.

The purpose of the program is to identify areas in geothermal processes where nonmetallic materials may be utilized in a cost-effective manner and to develop and test these materials under laboratory and field conditions. To date, polymer-concrete systems have been formulated, and laboratory and field tests have been performed in brine, flashing brine, and steam at temperatures up to 260°C. Data for exposure times of 2 years are available. Good durability is indicated. Economic studies indicate that use of these materials can result in ~10% reductions in power costs. Reductions up to ~37% in direct utilization processes also appear attainable.

Significant Accomplishments in 1978:

1. Long-term field testing was continued, and additional tests were started in several geothermal environments.
2. Prototype sections of polymer-concrete-lined pipe and vessels were placed into test.

3. An economic study was performed to determine the cost effectiveness of using nonmetallic materials in direct utilization geothermal processes. The results indicated cost reductions of 27 and 37% in sugar beet refining and barley malting processes, respectively.

Principal Activities Planned for 1979:

1. Field-testing programs currently in progress will be continued.
2. Refractory cements and other nonmetallic materials will be evaluated for possible use in geothermal environments.
3. High temperature sealing materials and joint designs will be developed.

Publications in 1978:

Journal Articles

Zeldin, A. N., Kukacka, L. E., Fontana, J. J., Carciello, N. R., and Reams, W. The influence of the curing agent concentration and curing temperatures on the thermostability of styrene-acrylonitrile-acrylamide-trimethylolpropane trimethacrylate copolymer systems. J. Appl. Polymer Sci. (submitted).

BNL Reports

Kukacka, L. E., Fontana, J., Zeldin, A., Sugama, T., Horn, W., Carciello, N., Amaro, J., and Reams, W. Alternate materials of construction for geothermal applications, progress report no. 15, October 1977-March 1978. BNL 50834 (April 1978).

Kukacka, L. E., Fontana, J., Zeldin, A., Amaro, J., Sugama, T., Carciello, N., and Reams, W. Alternate materials of construction for geothermal applications, progress report no. 16, April-September 1978. BNL 50925 (September 1978).

Kukacka, L. E., Fontana, J., Zeldin, A., Amaro, J., Sugama, T., Horn, W., Carciello, N., and Reams, W. Alternate materials of construction for geothermal applications, progress report no. 17, October-December 1978. BNL 50979.

Kukacka, L. E. The state-of-the-art of the use of concrete polymer materials for the repair of concrete hydrotechnical structures. BNL 24926 (September 1978).

Oral Presentations

Kukacka, L. E. Polymer concrete materials for geothermal processes. Presented at Plenary Lecture at U. S. DOE, Division of Geothermal Energy, Materials Symposium, Austin, Texas, May 22-25, 1978.

Kukacka, L. E. Polymer concrete materials for use in geothermal energy processes. Proc. Second International Congress on Polymers in Concrete, University of Texas at Austin, October 25-27, 1978, pp. 157-72.

CEMENTING OF GEOTHERMAL WELLS

FY 1978: \$500,000

Principal Investigator: L.E. Kukacka

FY 1979: \$376,000

Sponsor: Geothermal Energy (DOE)

Objective:

The objective of the program is to develop high temperature cementing materials for use in the completion of geothermal wells and deep oil and gas wells.

Scope:

Cementing of the well is considered to be the most critical single aspect in the development of a geothermal source. Portland or other forms of hydrated cement that are most widely used today do not exhibit good durability. Also, large variations in the cure time occur between batches of cement. Premature setting of the cement is not uncommon and results in plugging of the well, which necessitates costly redrilling.

Technical discussions with the geothermal industry indicated that a coordinated DOE-sponsored program for the development of cements designed specifically for geothermal applications was needed. To satisfy this need, BNL has developed and is managing a program on well-cementing materials. The program goals are being achieved by performance of the following tasks:

1. Development of inorganic and organic well-cementing materials capable of withstanding the environmental conditions in geothermal wells.
2. Development of the technology required to mix, pump, and place the cementing material.
3. Testing of the materials in down-hole test facilities.
4. Demonstration of the process by the cementing of prototype wells.

The work at BNL involves in-house research on polymer-concrete cementing materials as well as full management of an integrated program involving subcontract efforts and industrial participation.

Significant Accomplishments in 1978:

1. Technical management of the entire well cementing program was continued.
2. The definition phase of the program was completed.
3. The development of organic and inorganic cements was continued, several promising systems were identified, and property verification tests were started.
4. A cementing material was selected for use in the remedial cementing of a geothermal well.
5. An American Petroleum Institute-affiliated advisory committee on geothermal cements was organized.

Principal Activities Planned for 1979:

1. Technical management of the entire geothermal well cementing program will be continued.
2. In-house research on the development of polymer-concrete well cementing materials will be completed with the selection of a material and development of the placement technology.
3. The inorganic materials development phase of the program will be completed.

Publications in 1978:

BNL Reports

Kukacka, L. E., Fontana, J., Sugama, T., Rockett, T. J., Kalyoncu, R. S., Curtice, D. K., Fuller, E. R., Zeldin, A., Carciello, N., Reams, W., Kalousek, G. L., Simpson, B. E., and Roy, D. M. Cementing of geothermal wells, progress report no. 8, January-March 1978. BNL 50850 (May 1978).

Kukacka, L. E., Fontana, J., Sugama, T., Rockett, T. J., Kalyoncu, R. S., Zeldin, A., Curtice, D. K., Carciello, N., Kalousek, G. L., Simpson, B. E., and Roy, D. M. Cementing of geothermal wells, progress report no. 9, April-June 1978. BNL 50911 (September 1979).

Kukacka, L. E., Fontana, J., Sugama, T., Rockett, T. J., Kalyoncu, R. S., Curtice, D. K., Fuller, E. R., Zeldin, A., Carciello, N., Reams, W., Simpson, B. E., and Roy, D. M. Cementing of geothermal wells, progress report no. 10, July-September 1978. BNL 50943 (December 1977).

Oral Presentations

Zeldin, A., Kukacka, L. E., and Carciello, N. Concrete polymer materials for geothermal applications. Presented at AIChE Symposium, Philadelphia, Pennsylvania, June 4-8, 1978.

IMPLEMENTATION OF CONCRETE-POLYMER RESEARCH ON REPAIR OF
DETERIORATED CONCRETE

FY 1978: \$165,000

Principal Investigator: J.J. Fontana

FY 1979: \$130,000

Sponsor: Implementation Division,
Federal Highway Administration

Objective:

The objective of the program is to develop and transfer the technology necessary for the utilization of concrete-polymer materials in highway applications.

Scope:

The increased use of chloride deicing salts in recent years has resulted in the rapid deterioration of concrete bridge decks. Penetration of the chlorides into the concrete results in corrosion of the reinforcing steel. The corrosion increases the volume of the steel, which causes spalling and cracking of the concrete.

The high cost of repairing deteriorated bridge decks has resulted in a concerted research effort to find materials for the prevention and repair of such damage. This research has shown that concrete-polymers are among the materials that show promise in helping to alleviate this problem.

The current program provides the technical guidelines necessary for designated State highway agencies to use concrete-polymer materials successfully. The work involves the development and refinement of methods for using polymer materials under field conditions, and it includes working with State highway agencies to develop operational procedures for utilization of these materials.

Significant Accomplishments in 1978:

1. A large-scale demonstration of the use of concrete-polymer materials for the rehabilitation of a full bridge deck was completed by the New York State Department of Transportation with technical assistance from BNL.
2. The technology for the utilization of thin polymer-concrete overlay systems for bridge deck applications was developed, and field tests were performed.

3. A User's Manual describing procedures for the placement of thin polymer-concrete overlay systems was prepared and issued.

Principal Activities Planned for 1979:

1. The technology for the use of polymer-concrete to repair delaminated concrete will be developed.

2. The technical assistance effort will be expanded.

Publications in 1978:

BNL Reports

Webster, R., Fontana, J., and Kukacka, L. E. Thin polymer concrete overlays - interim user's manual. BNL 24110.

Oral Presentations

Webster, R. P., Fontana, J., and Kukacka, L. E. Rapid patching of concrete using polymer concrete. Presented at Continuously Reinforced Pavement Workshop, New Orleans, Louisiana, February 15-16, 1978.

Fontana, J. J., Webster, R., and Kukacka, L. E. Rapid patching of deteriorated concrete using polymer concrete. Presented at 2nd International Congress on Polymers in Concrete, Austin, Texas, October 25-27, 1978.

Fontana, J. J. and Webster, R. Thin sand filled resin overlays. Presented at 2nd International Congress on Polymers in Concrete, Austin, Texas, October 25-27, 1978.

IMPROVEMENT OF THE WEAR-RESISTANCE PROPERTIES
OF AGGREGATES BY MATERIALS IMPREGNATION

FY 1978: \$ 80,000

Principal Investigator: J.J. Fontana

FY 1979: \$130,000

Sponsor: Materials Division, Federal
Highway Administration

Objective:

The objective of the program is to select and evaluate materials and impregnation techniques for improving the wear-resistance properties of natural aggregates.

Scope:

In the interest of highway safety and energy conservation, it is essential that durable pavement surfacing systems with high skid resistance under severe traffic conditions be developed. For this application, high strength aggregate with a high resistance to polishing and weathering is required. The lack of availability of natural aggregates having these properties results in high shipping costs in many areas.

Earlier BNL work had shown that considerable improvement in the durability and strength of aggregate could be obtained by impregnation with organic and inorganic materials. Therefore, a composite consisting of a well-bonded plastic-like material dispersed in the vesicles or pores of an aggregate should be extremely durable. Under traffic conditions, the composite would be expected to wear differentially and thereby maintain its skid-resistance characteristics.

The current program includes the selection and evaluation of impregnation materials and processes, evaluation of the physical and mechanical properties of the treated aggregates, and small-scale field testing of promising systems.

Significant Accomplishments in 1978:

1. A literature survey was made on the characteristics of natural aggregates and potential impregnants, and a bibliography was compiled.
2. A total of 43 different aggregates were obtained from 11 states in various geological regions of the United States.

3. The preliminary phase of the research program was completed. This involved screening and evaluation of the 43 aggregates received and selection of four for further extensive testing.

4. The preliminary phase included tests to measure the wear resistance and polish resistance characteristics of the materials, before and after impregnation. Initial test results indicate that impregnation significantly increases the wear resistance of aggregates and reduces the depth of wear, but has no significant effect on their polish resistance.

Principal Activities Planned for 1979:

1. The selection and evaluation of inorganic and organic materials and processes for use in the production of impregnated aggregate will continue.

2. The characterization of natural and impregnated aggregates will be continued. Properties to be evaluated will include micro-texture, affinity for binders, resistance to weathering, polishability, and wear resistance.

3. Circular track-type accelerated wear-polish tests will be performed on pavement mixtures containing the most promising impregnated aggregate.

4. The economics of aggregate impregnation will be analyzed in terms of cost and availability of the impregnant, estimated processing costs, and the relation of these factors to potential markets for use of impregnated aggregates.

Publications in 1978:

Oral Presentations

Webster, R. P. and Fontana, J. J. Improvement of wear-resistance properties of natural aggregates by materials impregnation. Presented at the 1978 FCP Research Review Conference, College Park, Maryland, October 3-6, 1978.

DEVELOPMENT OF A GLASS-POLYMER COMPOSITE SEWER PIPE FROM WASTE GLASS

FY 1978: \$100,000

Principal Investigator: L.E. Kukacka

FY 1979: \$ 30,000

Sponsor: Industrial Energy Conservation
(DOE)

Objective:

The objective of this program is to provide the technical basis for energy conservation by the development, testing, and practical demonstration of products made from waste glass.

Scope:

At present, uses for recycled ferrous and nonferrous metals are apparent, but efficient methods for utilizing other components of urban waste, such as glass and paper, are needed. This program involves the development, testing, and practical demonstration of products made from waste glass.

Experiments have shown that glass can be incorporated into composite materials used for construction. Glass-polymer composite sewer pipe containing glass separated from urban waste has been produced and is currently being field-tested in two sewage systems. Other potential applications include building blocks, chemical storage tanks, and energy storage devices.

The properties of the composite pipe have been determined to a degree that they are statistically acceptable for application to relevant ASTM methods and standards. The results indicate that, compared with several ASTM classes of steel-reinforced concrete pipe, glass-polymer composite (GPC) pipe is strong enough to eliminate the need for steel and allows reduction of the wall thickness by 30 to 50%. Its use also provides significant reductions in energy consumption and cost.

Significant Accomplishments in 1978:

1. Studies to optimize the glass particle size distribution with respect to the physical properties of GPC pipe resulted in reductions in the required polymer content from 12.5 to 10.2 wt%, leading to significant cost reductions and energy conservation benefits.

2. Durability testing of GPC, reinforced concrete, vitrified clay, and asbestos cement sewer pipe in acid and hot aqueous environments was started.

3. Full-scale pipe sections were installed in a sewage system for test in a pH 2.4 environment.

Principal Activities Planned for 1979:

1. Long-term durability testing will be completed.
2. A final report will be prepared.

Publications in 1978:

BNL Reports

Kukacka, L. E., Fontana, J., Rayfiel, R., Arnold, G., and Galen, B. Development of a glass polymer composite sewer pipe from waste glass, progress report no. 7, January-March 1978. BNL 50835.

Kukacka, L. E., Fontana, J., Rayfiel, R., Arnold, G., and Galen, B. Development of a glass polymer composite sewer pipe from waste glass, progress report no. 8, April-June 1978. BNL 50886.

FLASH HYDROPYROLYSIS OF COAL

FY 1978: \$257,000

Principal Investigators: M. Steinberg
P. Fallon

FY 1979: \$300,000

Sponsor: Fossil Energy (DOE)

Objective:

The objective of this program is to obtain process chemistry information required for the development of processes involving the flash hydropyrolysis of coal for conversion to liquid and gaseous hydrocarbon products.

Scope:

The flash hydropyrolysis of coal is a rapid gas-phase, noncatalytic, direct hydrogenation technique for conversion of coal to both liquid and gaseous hydrocarbon products. The needed process chemistry information includes the yield and distribution of products as a function of the process variables, such as reactor temperature and pressure, coal type and residence time at reactor conditions, and feed gas composition. The technical approach is to contact finely divided coal particles with hot hydrogen at elevated pressure and temperature; this fractures the polycyclic structure of the coal molecule and adds hydrogen, increasing the H/C ratio. The products formed are then rapidly quenched to prevent decomposition and recombination. The equipment used is an entrained down-flow tubular reactor system capable of feeding up to 2 lb/hr of coal and operating at pressures up to 4000 psi and temperatures up to 900°C. Sample taps located at 2-ft intervals along the length of the 8-ft reactor allow product samples to be taken for studying the effect of residence time. Product analysis is obtained with a programmable on-line gas chromatograph, calibrated to measure CO, CO₂, CH₄, C₂H₆, and BTX (benzene, toluene, and xylene) concentrations every 8 minutes. Liquid products heavier than C₉ are collected in product condensers and characterized and measured at the termination of each experiment. Data reduction and correlation are computerized, and the information is applied to a kinetic model of the overall reaction. Preliminary process design and analysis are also performed.

Significant Accomplishment in 1978:

1. Approximately 100 experimental runs were conducted, primarily with a noncaking lignite. The equipment was operated successfully up to its maximum design conditions of 4000 psi hydrogen pressure and 900°C.
2. Although the tests included all conditions of pressure and temperature, emphasis was on conditions that would maximize either liquid yields or gaseous yields. The liquid yields were maximum at 775°C and 2000 psi, with 10% carbon conversion to benzene and 10% to light oils, for a total of 20%. The gas yields were maximum at 875°C and 2500 psi, with up to 90% carbon conversion to methane and ethane.
3. Samples from the taps along the length of the reactor provided considerable information about the effect of residence time on these products. Coal residence time ranged from 1 to 10 sec in the reaction zone.
4. The effect of coal heat-up rate was studied both by use of the hydrogen preheater and by varying the temperature profile along the length of the reactor.
5. A number of exploratory runs were done with treated caking coal, sub-bituminous coal, recycled char, and iron-catalyst-impregnated lignite.
6. The information obtained on lignite was correlated by using a kinetic model of the overall reaction, and expressions for the rate of reaction were developed for use in reactor engineering.
7. Preliminary process design and analyses for a motor fuel coal conversion plant and a chemical feedstock plant were performed.

Principal Activities Planned for 1979:

1. The process chemistry studies of the rapid hydrogenation reaction will be done primarily with a sub-bituminous coal. Experiments will be done also with various treated and untreated bituminous coals.
2. Emphasis will be on increasing the yield and concentration of methane in the process stream so as to approach thermodynamic equilibrium values.
3. Other feed gases, such as CO-H₂ mixtures, will be used to simulate recirculating process gas.

4. Kinetic modeling and data correlations will be kept up to date as more information becomes available. Process design and economic evaluations will continue to an extent depending on budgetary restraints.

5. Exploratory runs on catalyst additives to lignite and bituminous coals will be conducted with the objective of improving the liquid yields.

Publications for 1978:

BNL Reports

Steinberg, M. and Fallon, P. Flash hydrolysis of coal, progress report no. 5, January-March 31, 1978. BNL 50894 (August 1977).

Steinberg, M. and Fallon, P. Flash hydrolysis of coal, progress report no. 6, April 1-June 30, 1978. BNL 50948 (December 1978).

Oral Presentations

Steinberg, M., Fallon, P., Dang, V., Ziegler, E., and Lee, Q. Reaction process and cost engineering for the flash hydrolysis (FHP) of coal. Presented at 71st Annual Meeting of American Institute of Chemical Engineers, Miami, Florida, November 12-16, 1978.

ALTERNATIVE PROCESS SCHEMES FOR COAL CONVERSION

FY 1978: ---

Principal Investigator: M. Sansone

FY 1979: \$100,000

Sponsor: Fossil Energy (DOE)

Objective:

The purpose of this program is to suggest improvements to existing and developing processes for conversion of coal to hydrocarbon fuels and to identify and initiate studies on potentially attractive new conversion concepts.

Scope:

Present coal conversion (gasification and liquefaction) and product recovery processes are subject to thermal and coal utilization inefficiencies and have high capital costs; the production cost for the gaseous and liquid hydrocarbon products is therefore high. Improved processes are needed for recovery of product gas and liquid and for recycling of process streams. The initial efforts involve assessment of two major areas for potential energy savings: (1) catalytic gasification and direct gasification (hydrogasification) and (2) product gas separation techniques. The studies will include (1) process chemistry and flow sheet development, (2) preliminary process design, i.e., mass and energy balances, and (3) preliminary economic evaluation. New conversion approaches will also be investigated and exploratory experiments will be initiated in areas which show technical promise but may lack data demonstrating feasibility.

Significant Accomplishments in 1978:

This study was initiated in October 1, 1978.

Principal Activities Planned for 1979:

1. The catalytic hydrogasification of coal will be reviewed. An example of this is the Exxon system, in which a gaseous mix of H_2 , CO, and CH_4 is produced. Methods of separation of product CH_4 (pipeline gas) from H_2 and CO, which are recycled, will be investigated.

2. The flash hydrolysis of coal will be reviewed. This process, when operating in the gasification mode, produces a gaseous mix of H_2 , CH_4 , and C_2H_6 . Methods of separating the CH_4 and C_2H_6 (high-Btu pipeline gas) from the H_2 , which is recycled, will be studied.

3. These gaseous separation methods will include (a) absorption/stripping, (b) membrane diffusion, (c) adsorption, (d) cryogenic, and (e) hydrate formation.

4. Conceptual designs of alternative gaseous and liquid phase coal conversion processes will be investigated.

Publications in 1978:

No. publications. This study was initiated in October 1, 1978.

REGENERATIVE PROCESS FOR DESULFURIZATION OF HIGH TEMPERATURE
COMBUSTION AND FUEL GASES

FY 1978: \$357,000

Principal Investigators: M.S. Shen
A.S. Albanese

FY 1979: \$250,000

Sponsor: Fossil Energy (DOE)

Objective:

The purpose of this program is to obtain basic process chemistry information required for the development of processes for the regeneration of limestone or lime-based sorbent used in the desulfurization of combustion and fuel gases in power production cycles. Application of such regeneration to fluidized-bed combustion (FBC) of coal is the specific goal.

Scope:

A major advantage of fluidized-bed combustion is that it can produce a desulfurized hot gas from coal combustion if lime is used. However, economic and environmental considerations require regeneration of lime from the calcium sulfate formed, and no satisfactory process for this has yet been developed.

The research and development approach to studying regenerable sorbents for FBC includes (1) identification of new regenerable SO₂ sorbents for FBC, and obtaining of information on the rate and capacity of sulfation and regeneration for both fresh and cycled sorbent, (2) preparation of sorbent pellets of a size suitable for use in fluidized-bed combustors and having acceptable reactivity and high resistance to attrition, (3) operation of bench-scale sorbent regeneration equipment (kiln and fluidized beds), (4) clarification of the physical and chemical factors that account for differences in reactivity among various sorbents, and (5) evaluation of process design and economics with a view to commercial development of new sorbents on the basis of experimental data developed in the program.

Significant Accomplishments in 1978:

1. Calcium silicates were found to be far superior to standard limestone, and their sulfation and regeneration capabilities are being further studied.

2. Laboratory studies on the preparation of active calcium silicates and on silica-supported sorbent were initiated.

3. A bench-scale kiln test of the BNL regeneration process (regeneration of CaO by roasting CaSO_4 and fly ash, which contains 20% unburnt carbon, in a kiln) was completed. It included measurement of the effects of flow rate, temperature, and solids loading on effluent SO_2 concentration and on regeneration rate, both under isothermal conditions and with external heating.

4. A simple mathematical model was derived to describe the reactor performance. The kinetic parameters for both $\text{CaSO}_4 + \text{CaS}$ and $\text{CaSO}_4 + \text{C}$ reactions were also obtained.

5. Iron oxide catalysis of the sulfation and regeneration of limestone or lime-based sorbents was investigated and found to improve the rate processes significantly.

6. A process design and economic analysis of the BNL kiln regeneration process was prepared and compared with that of a once-through limestone system.

Principal Activities Planned for 1979:

1. Laboratory study on the low-cost production of active calcium silicates will continue.

2. Laboratory studies on the sulfation and regeneration of the active calcium silicates and the silica-supported sorbent will continue.

3. Laboratory studies on the sulfation and regeneration of calcium silicate based sorbents, such as portland cements, will be initiated.

4. Catalyzed sulfation and regeneration of calcium silicates and cements will be investigated.

5. A 3-in.-i.d. rotary kiln will be constructed, equipped for external heating and continuous solid feeding (1 lb/hr). Parametric studies of the BNL regeneration process will be made.

6. Screening and testing of low cost binders for limestone fines and calcium silicates will be initiated, with the aim of improving the sulfur sorption reactivity and the resistance to attrition of these sorbents.

Publications in 1978:

Journal Articles

Yang, R. T., Shen, M., and Steinberg, M. Fluidized-bed combustion of coal with lime additives. Catalytic sulfation of lime with iron compounds and coal ash. *Env. Sci. Tech.* 12, 915 (1978).

Yang, R. T. and Shen, M. A regenerative process for fluidized-bed combustion of coal with lime additives. *Ind. Eng. Chem. Process Des. Dev.* (in press).

Chen, J. M. and Yang, R. T. Fluidized-bed combustion of coal with lime additives. Kinetics and mechanism of regeneration of the lime sorbent. *Ind. Eng. Chem. Fundamentals* (in press).

Shen, M. and Yang, R. T. Direct evidence for the existence of gaseous intermediates in the CaS-CaSO_4 reaction. *AIChE Journal R&D Notes* (in press).

Yang, R. T. and Chen, J. M. Kinetics of desulfurization of hot fuel gas with calcium oxide. Reaction between COS and CaO. *Env. Sci. Tech.* (in press).

Yang, R. T. and Shen, M. Catalytic fluidized-bed combustion of coal. Enhancement of sulfation and regeneration of calcium oxide by iron oxide. *Ind. Eng. Chem. Proc. Des. Dev.* (submitted).

Chen, J. M. and Yang, R. T. Modelling and kinetic studies of a rotary kiln reactor: Regeneration of sorbent for fluidized-bed combustion. *Chem. Eng. Sci.* (submitted).

Yang, R. T. and Shen, M. Calcium silicates - A new class of highly regenerative sorbents for hot gas desulfurization. *AIChE Journal* (submitted).

BNL Reports

Yang, R. T., Albanese, A. S., Chen, J. M., Farber, G., Kainz, F. B., Pruzansky, J., Shen, M-S., and Steinberg, M. Regenerative process for desulfurization of high temperature combustion and fuel gases, progress report no. 7, October 1-December 31, 1977. BNL 50809 (February 1978).

Yang, R. T., Albanese, A. S., Chen, J. M., Farber, G., Kainz, F. B., Pruzansky, J., Shen, M-S., Steen, C. L., and Steinberg, M. Regenerative process for desulfurization of high temperature combustion and fuel gases, progress report no. 8, January 1-March 31, 1978. BNL 50866 (May 1978).

BNL Reports (Cont'd)

Yang, R. T., Albanese, A. S., Chen, J. M., Farber, G., Kainz, F. B., Pruzansky, J., Shen, M-S., and Steinberg, M. Regenerative process for desulfurization of high temperature combustion and fuel gases, progress report no. 9, April 1-June 30, 1978. BNL 50891 (August 1978).

Albanese, A. S., Chen, J. M., Farber, G., Kainz, F. B., Pruzansky, J., Shen, M-S., and Steinberg, M. Regenerative process for desulfurization of high temperature combustion and fuel gases, progress report no. 10, July 1-September 30, 1978. BNL 50944 (December 1978).

CONSERVATION IN THE ETHYLENE POLYMER INDUSTRY —
POLYKETONES AND POLYSULFONES

FY 1978: \$ 90,000

Principal Investigators: M. Steinberg
R. Johnson

FY 1979: \$100,000

Sponsor: Industrial Energy Conservation
(DOE)

Objective:

The objectives of this program are to develop useful energy-conserving polymers, particularly polyketones and polysulfones, and a process for their manufacture for the plastics industry.

Scope:

The program is being carried out at BNL in cooperation with an industrial company (Tenneco). It was shown previously at BNL that CO can be incorporated into ethylene to produce polyketone polymers, and SO₂ to produce polysulfone polymers, by a high energy radiation technique. These polymers offer a major potential for conserving valuable ethylene raw material and energy in the polyethylene market. CO and SO₂ are, respectively, low cost and waste raw materials. Estimates indicate a conservation potential of two billion pounds of ethylene, or 25% of the overall U.S. market, by substituting CO and SO₂, assuming 50% penetration of the bulk polyethylene market. The savings amount to more than \$280 million per year at current market prices. The saving in energy alone amounts to a substantial 0.1 Quad/yr equivalent and at least 100 billion cubic feet/yr of natural gas. The use of machine radiation may be preferred because of its possible unique process chemistry, safety, availability, and low initial investment. The project focuses on the following three major tasks: (1) establishment of the uniqueness of the radiation process, (2) determination of the processability and marketability of the substituted copolymers, and (3) design, construction, and operation of a pilot plant for producing the substituted ethylene copolymers. This project is in support of a program being conducted by Tenneco Inc. under a separate agreement with DOE. BNL is to provide technical and supervisory assistance to Tenneco in the form of basic

experimental and process information, equipment, and laboratory facilities. Tenneco Inc. is to provide polymer characterization and formulation, marketing expertise, and scientific and technical assistance to BNL.

Significant Accomplishments in 1978:

1. A series of ethylene-carbon monoxide copolymers were prepared by ^{60}Co gamma radiation induction and by chemical catalysis. Compositions ranging from 41 to 49% CO were obtained. The copolymers containing ~50% CO prepared by ^{60}Co gamma radiation have significantly better mechanical properties than do copolymers prepared by conventional free-radical catalysis.
2. Electron-beam machine radiation was used for the first time to produce ethylene-CO copolymers. The G-values (molecules polymerized/100 eV deposited) appear to be lower than for ^{60}Co gamma radiation.
3. Ethylene-SO₂ copolymers were produced with electron-beam machines. The G-values appear to be very high (>10,000) and are independent of the type of radiation. A strong post-irradiation polymerization effect is observed.
4. An ethylene-CO-SO₂ terpolymer has been produced for the first time.

Principal Activities Planned for 1979:

1. Pound quantities of ethylene-CO copolymers will be prepared with ^{60}Co gamma radiation.
2. In conjunction with Tenneco Inc., the properties of these ethylene-CO copolymers will be characterized and evaluated.
3. The properties of copolymers produced by irradiation under different pressure conditions will be determined and compared with those of thermocatalytically produced copolymers.
4. A program on production of ethylene-SO₂ copolymers with another industrial firm will be initiated.

Publications in 1978:

BNL Reports

Steinberg, M., Johnson, R., Colombo, P., Cordes, W., Koral, M., and Goodman, D. Polyketones and polysulfones for conservation in the ethylene polymer industry, progress report no. 1, October 1977-March 1978. BNL 50884 (May 1978).

BNL Reports (Cont'd)

Steinberg, M., Johnson, R., Cordes, W., and Goodman, D. Polyketones and polysulfones for conservation in the ethylene polymer industry, progress report no. 2, April-September 1978. BNL 50955 (December 1978).

Oral Presentations

Steinberg, M., Johnson, R., Cordes, W., and Goodman, D. Polyketones in the ethylene polymer industry. Presented at the 2nd International Meeting on Radiation Processing, Miami, Florida, October 22-26, 1978; Proceedings (in press).

ENVIRONMENTAL CONTROL TECHNOLOGIES:

(1) FHP OF COAL AND (2) ATMOSPHERIC CO₂ CONTROL

FY 1978: \$65,000

Principal Investigators: A.S. Albanese

FY 1979: \$70,000

Sponsor: Environmental Control Technology
(DOE)

Objective:

The purpose of this two-part program is (1) to assess the environmental control technologies (ECTs) for the flash hydrolysis (FHP) of coal and (2) to assess the possibilities of controlling the increase of CO₂ in the atmosphere.

Scope:

For investigating the FHP of coal in terms of environmental control, the approach is to conduct laboratory analyses on samples obtained from the BNL experimental FHP tubular reactor unit currently in operation, and, on the basis of the experimental data, prepare conceptual flow diagrams, including mass and energy balances, of full-scale FHP-chemical and FHP-refinery complexes. The results will provide an indication of the possible effluents from integrated FHP complexes, provide a basis for establishing environmental guidelines for FHP and related processes, and identify areas in which new control technologies are required for commercialization of the process.

For investigating the possible environmental control of the global CO₂ problem, literature data are assembled, and the findings for CO₂ emissions and concentration levels are correlated. A systematic study is then made of the possible removal, recovery, disposal, and reuse of the CO₂. The effects of substitution of alternative fuels are investigated.

Significant Accomplishments in 1978:

FHP

1. The organic liquid product of the FHP experimental unit was analyzed for polynuclear aromatic hydrocarbons, carbon, hydrogen, nitrogen, sulfur, and trace elements.
2. The elemental compositions and volatile matter contents of coal feed and char product were determined for a number of experimental runs.

3. Conceptual process flow plans (including material balances) and environmental assessment of FHP-chemical and FHP-refinery complexes were prepared.

CO₂

1. A compilation of the historical data on CO₂ buildup in the atmosphere was reviewed, and a preliminary assessment of methods of controlling atmospheric CO₂ was completed.

Principal Activities Planned for 1979:

FHP

1. An economic evaluation of the FHP-chemical and FHP-refinery complexes will be completed, and the costs of pollution control equipment will be identified.

2. Experimental analyses on FHP effluents will be continued.

3. Available data on processes related to the FHP process (e.g., IGT at Rocketdyne) will be analyzed. Similarities and common problem areas, as well as significant differences in the process effluents and required control technologies, will be identified.

CO₂

1. A literature survey will be made, and findings on CO₂ emissions and atmospheric concentration levels will be consolidated.

2. Conceptual processing schemes for CO₂ recovery, recycle, reuse, and disposal will be prepared.

3. Evaluation studies will be performed and conclusions reported.

Publications in 1978:

BNL Reports

Steinberg, M. and Albanese, A. S. Environmental control technology for the flash hydrolysis of coal, progress report no. 1, June 20, 1977 to September 30, 1977. BNL 50873 (January 1978).

Steinberg, M., Albanese, A. S., and Dang, V. D. Environmental control technology for atmospheric carbon dioxide, progress report no. 1, June 20, 1977 to September 30, 1977. BNL 50794 (January 1978).

BNL Reports (Cont'd)

Steinberg, M. and Albanese, A. S. Environmental control technology for atmospheric carbon dioxide, progress report no. 2, October 1, 1977-March 31, 1978. BNL 50877 (July 1978).

Steinberg, M. and Steinberg, M. Environmental control technology for the flash hydrolysis of coal, progress report no. 2, October 1, 1977-March 31, 1978. BNL 50906 (September 1978).

Oral Presentations

Steinberg, M., Albanese, A., and Dang, V. D. Environmental control technology for carbon dioxide. Presented at 71st Annual Meeting of American Institute of Chemical Engineers, Miami, Florida, November 12-16, 1978.

PROGRAMS PROPOSED FOR INITIATION IN FY 1980

In addition to the programs summarized above, the Process Sciences Division has proposed to undertake two new programs in FY 1980:

High Efficiency Chemical Processes and Power Cycles Involving CO₂
Recycle

Synthetic Fuel Using Non-Fossil Energy Sources