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**PROGRAM SUMMARIES FOR 1979 -
ENERGY SCIENCES PROGRAMS**

MASTER

December 1979

DEPARTMENT OF ENERGY AND ENVIRONMENT

**BROOKHAVEN NATIONAL LABORATORY
UPTON, NEW YORK 11973**

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PROGRAM SUMMARIES FOR 1979 - ENERGY SCIENCES PROGRAMS

B. MANOWITZ, Chairman
D.H. GURINSKY, Coordinator for Energy Sciences

December 1979

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ABSTRACT

This report describes the objectives of the various research programs that constitute the Energy Sciences activities of the Department of Energy and Environment, along with some of their more significant accomplishments during 1979. Information concerning budget totals for FY 1979 and FY 1980, Principal Investigator(s), and publications for the period covered is also given for each program.

Plans for 1980 are described.

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* Work being performed in the Environmental Chemistry Division

** Work being performed in the Department of Nuclear Energy

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INTRODUCTION

The Energy Sciences activities of the 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 Division

Metallurgy and Materials Science Division

Process Sciences Division

The Divisions are primarily administrative structures that provide greater cohesion and guidance to activities that naturally share common scientific approaches to specific problems. Each Division might be characterized by its individual main focus. Thus, in the Chemical Sciences Division the main focus is on basic chemistry; in the Metallurgy and Materials Science Division, on basic and applied materials research; and in the Process Sciences Division, on applied chemistry and chemical engineering.

The free flow of ideas and information across Divisional lines is fostered and occurs. There are a number of instances of complementary and interrelated programmatic interests not only among programs within a Division, but 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. It is expected that work performed in the Energy Sciences area will lead to the identification of ideas that are appropriate for further development in either the Energy Technology area of the Department or elsewhere. Several instances of such movement of ideas 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; (3) applied research on polymer-impregnated concrete leading to a development program on the use of these materials for highway service and geothermal well applications.

The formal organizational relationships that exist among the Divisions of the Energy Sciences area, as well as those that exist among the other areas of the Department, are illustrated in the accompanying organizational chart.

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CHEMICAL SCIENCES DIVISION

Donald J. Metz

The programs of the Chemical Sciences Division focus on understanding 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; coal conversion and liquefaction; hydrogen generation and storage; combustion of alternative fuels; catalysis; fuel recovery and separation of hazardous wastes; nitrogen fixation; advanced battery development and two-phase fluid dynamics.

The programs represent a broad spectrum of both subject matter and investigative approach. 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 in chemical reactions pertinent to energy-related programs;
- 2) developing reliable techniques that are applicable to systems of concern in energy generation, conversion, or storage and in the control of the processes involved.

SIGNIFICANT ACCOMPLISHMENTS

Listed below are a selection of significant accomplishments in the Chemical Sciences Divisions's programs during 1979. Details of the technical progress achieved in that period in each program are more fully documented in published reports and budget submission documents.

In the Porphyrin Chemistry program, picosecond kinetic data on diporphyrins cofacially linked approximately $4 \text{ \AA}$ apart provided additional evidence for the mechanism proposed for the transduction of light into chemical oxidants and reductants in photosystem II (oxygen evolution in plants). These experiments demonstrate that synthetic manipulation of donor to acceptor distances, orientation, and redox characteristics leads to photoinduced charge separation in an artificial system with kinetics and thermodynamic efficiencies that approach those found in photosynthetic organisms. Also in this program, the first direct determination of the structure of a bacteriochlorophyll derivative was accomplished by x-ray diffraction.

In the investigation of the Kinetics and Mechanisms of Chemical Processes Related to the Development and Use of Energy, it was demonstrated that an excimer (excited dimer complex) produced in pyrene adsorbed on porous glass had a decay lifetime $\sim 10^3$ times longer than the corresponding excimer formed in pyrene in solution.

In the Energetic Compounds study, a correlation between the electrode potentials of singly and multiply bridged ferrocenes and the number of C-H bonds in the bridges (more specifically in the field of the iron atom) was established.

The Kinetics and Mechanisms of Alternative Fuels Combustion program successfully operated its discharge flow-resonance fluorescence apparatus at temperatures up to 1150K and obtained results for reactions of ground state atomic oxygen with methane and ethane. These temperatures are the highest attained to date to make direct measurements of absolute rate constants for elementary reactions in a conventional fast flow reactor.

In the Bioelectrochemistry and Electrochemistry program, it was unequivocally demonstrated that a bilayer lipid membrane (glycerol monolein) doped with either magnesium etiochlorin or magnesium mesochlorin didodecylamide facilitates transport of electrons between two aqueous phases.

The Metal Hydrides study showed that the partial molar volume of hydrogen in several metal alloy hydrides is anomalously low and variable. This is felt to be direct experimental evidence that there is preferential occupation by hydrogen of defect sites produced by either surface segregation (e.g., LaNi_5) and/or non-stoichiometry (e.g., $\text{TiCr}_{1.8}$).

In the High Temperature Chemistry program, a detailed study of the electrical conductivity of $\text{Li}_{3+\delta}\text{Sb}$, a compound semiconductor, was made as a function of Li content, the latter being controlled by coulometric titration. Conductivity was a minimum at $\delta = -1.0 \times 10^{-3}$ and changed over four orders of magnitude for $-0.004 < \delta < +0.004$. Analysis of the data yielded such parameters of the system as electron and electron hole concentrations and mobilities, as well as effective masses, and band gap at 355°C .

In the study of hydrogenation/dehydrogenation reactions undertaken in the Chemistry and Physics of Coal Utilization program, the mechanism of the gas phase transformation of tetralin to anthracene was established, along with the relevant Arrhenius parameters. Quite unexpectedly, it was also established that the pyrolysis of bibenzyl in liquid tetralin is much more complicated than previously stated in that, in addition to bond cleavage and reduction to toluene, dehydrogenation to stilbene also occurs.

The Investigation of Carbon Oxide Reactions found that surface oxidized metals that form strong metal-oxygen bonds (e.g., Ti, W, Zr) decomposed ethylene glycol to ethylene and effected the inter-molecular coupling of benzophenone to form tetraphenylethylene.

The Cyclic Separations Process Research study succeeded in identifying the mechanism of gas phase hydrogen isotope separation via pressure and temperature swing processes when using a metal hydride as the solid substrate.

The Trace Element Analysis Using Synchrotron Radiation study initiated a ray tracing program designed to provide design information for the construction of an x-ray microprobe beam line. The program is expected to be used in the design of other beam lines by the NSLS.

Title: Porphyrin Chemistry

FY 79: \$463,000

Principal Investigator:
J. Fajer

FY 80: \$490,000

Sponsor: Basic Energy
Sciences (DOE)

This work represents a multi-disciplinary program which involves synthetic, structural, theoretical, and physical chemistry and addresses 1) the role of porphyrins and their radicals in the transduction of light into chemical energy in photosynthesis and 2) applications of these reactions to solar energy conversion by generation of electricity via photo-excitation of porphyrins deposited on solid interfaces or isolated in films and micelles, the production of hydrogen and oxygen using porphyrins to mimic the photosynthetic apparatus and decompose water, and the fixation of carbon compounds photochemically via porphyrin derivatives.

The results obtained regarding the electronic structure and chemical properties of the chlorophylls involved in photosynthesis are directly applicable to vital metabolic reactions, also mediated by porphyrins, such as oxygen and electron transport, hydroxylations, peroxide decomposition, and nitrite and sulfite assimilation. This work, therefore, also aims at determining metabolic mechanisms in order to develop photo-assisted and electrochemical catalytic systems based on porphyrins for oxygen reduction (fuel cells), regiospecific chemical syntheses, and nitrogen fixation.

The methods used to study these reactions, which involve oxidation-reduction mechanisms, include techniques such as optical, photoacoustic, and picosecond spectroscopy, electron spin resonance (ESR), nuclear magnetic resonance (NMR), and electron nuclear double resonance (ENDOR). Structural parameters for the compounds under investigation are obtained by x-ray and neutron diffraction, extended x-ray absorption fine structure (EXAFS), x-ray photo-electron spectroscopy and single crystal polarized microspectrophotometry. The redox reactions are induced chemically, photochemically, and electrochemically, and the chemistry is

guided by theoretical calculations used to predict the chemical properties of model systems. These, in turn, are used to establish the role of the porphyrins in photosynthesis and biochemical catalysis, and use them in biomimetic energy transduction.

Publications

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- BNL 26302^a K. M. Barkigia, J. Fajer, and G. J. B. Williams, "The Crystal and Molecular Structure of $\alpha,\beta,\gamma,\delta$ -Tetrapropylporphyrinato Lead(II)," American Crystallographic Association Meeting, Boston, Massachusetts, August 17-21, 1979.

^a Abstract

Title: Kinetics and Mechanisms of Chemical Processes Related to the Development and Use of Energy

FY 79: \$170,000

Principal Investigator:
J. W. Sutherland

FY 80: \$180,000

Sponsor: Basic Energy
Sciences (DOE)

The objective of this program is to develop basic kinetic and mechanistic information about selected chemical systems which are associated with the development and use of energy sources and for which present data are inadequate or unavailable. Short-lived transient chemical species are characterized by flash photolytic and pulse radiolytic techniques, while steady-state photolytic, steady-state radiolytic and standard kinetic methods are used to identify and measure yields of final products of a particular overall reaction. Principal topics being investigated are the photochemistry of selected molecules adsorbed on high surface area solids and the chemistry of transient nitrogen compounds. Some aspects of the reactivity of sulphur dioxide are also being studied. Information developed in this program is relevant to investigations into systems being considered for the photochemical conversion and storage of solar energy, into methods for nitrogen fixation, and to problems in sulphur chemistry associated with the development and use of geothermal energy sources and of fossil fuels. The results of this investigation, in addition to their intrinsic value to the general field of chemical kinetics, are available as quantitative input data for models designed to assess the impacts of using various energy sources.

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James W. Sutherland, "Pulse Radiolysis of Aqueous Hydrazine Solutions. The Triazene Species," J. Phys. Chem. 83, 789-795 (1979).

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Reports:

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^a Abstract

Title: Investigation of the Chemistry of Energetic Compounds

FY 79: \$164,000

Principal Investigator:
M. Hillman

FY 80: \$175,000

Sponsor: Basic Energy
Sciences (DOE)

This program is an investigation of the preparation, structure, and chemistry of energetic compounds. Energetic compounds have the property that they may undergo certain types of reactions that ordinary compounds will not. Examples of these properties include such phenomena as ability to catalyze other reactions, the ability to become electrical conductors under the influence of light, and the ability to partake in chemical reactions 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 photochemistry, this project includes the possibility of decomposition of water. In the area of conductivity, this project includes the possibilities of both photoconductivity and superconductivity in organic molecules. In the realms of photochemistry and photoconductivity, of particular interest are intensely colored derivatives of compounds capable of partaking in intermolecular electron transfer reactions. Ferrocene derivatives exist with a wide range of conductivities. They also have been shown to form intensely colored compounds. Photosensitive molecules may prove of practical interest in developing use of solar energy.

Publications

Reports:

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^a Abstract

- BNL 16521 M. Hillman, "Chemical Effects of Nuclear Transformations. Inorganic Compounds in Solution," in Chemical Effects of Nuclear Transformations in Inorganic Systems, G. Harbottle and A. G. Maddock, editors, North-Holland Publishing Co., Chapter 5, 1979.
- BNL 26497 Manny Hillman, Etsuko Fujita, and Masao Hisatome, "Bridged Ferrocenes VI. PMR Spectra - Conformations and Oscillations," submitted for publication in J. Organometal. Chem.
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Title: Kinetics and Mechanisms of Alternative Fuels Combustion

FY 79: \$255,000

Principal Investigator:
R. B. Klemm

FY 80: \$275,000

Sponsor: Basic Energy
Sciences (DOE)

The objective of this task is to investigate the chemical kinetic and mechanistic factors involved in gas phase combustion and pollutant formation processes. Particular emphasis is placed on alternative fuels which comprise a wide range of fuel types, including methyl and ethyl alcohol, synthetic hydrocarbons, and hydrogen. These fuels are not yet in wide use, but their potential for utilization is significant since most can be derived from coal or biomass. This task addresses technical aspects of the alternative fuels question, such as combustion efficiency and pollutant emission rates, at a fundamental level. Two complementary techniques are applied to determine specific rates for combustion related, elementary atom-molecule reactions, viz., that of flash photolysis-resonance fluorescence (220-520 K) and discharge flow-resonance fluorescence (295-1150 K). Combined, these experimental methods provide an unusually wide temperature span, ~ 200-1200 K, over which to study the kinetics of combustion initiation reactions and oxidation reactions of combustion intermediates. These techniques complement one another and thus reinforce the validity of the experimental results. In addition, a photo-ionization mass spectrometer (PIMS) experiment that utilizes the National Synchrotron Light Source is being developed jointly between the Department of Energy and Environment and the Chemistry Department. The PIMS apparatus is employed in this task to examine molecular beams sampled from a low pressure, premixed flame. Concentration profiles of radical and stable flame species are modelled using independently derived elementary rate data to provide mechanistic information for high temperature systems.

Publications

Journal Articles and Conference Proceedings:

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Reports:

- BNL 26149^a Tsuneo Tanzawa and R. Bruce Klemm, "A Modeling Study of the Reaction of O(³P) with H₂CO," 178th Annual Meeting of the American Chemical Society, Washington, D.C., Sept. 9-14, 1979.
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- BNL 27004 J. R. Grover, R. B. Klemm, and J. B. A. Mitchell, editors, "Report of Workshop on Windowless Gas Phase Beam Line at the National Synchrotron Light Source," WGPBL Workshop, Upton, New York, June 29, 1979.

^a Abstract

Title: Bioelectrochemistry and Electrochemistry

FY 79: \$155,000

Principal Investigator:
S. W. Feldberg

FY 80: \$165,000

Sponsor: Basic Energy
Sciences (DOE)

The long range objective of this program is the ultimate understanding of how light energy can be converted to useful work by taking advantage of the unique structure and organization of ultrathin ($< 100 \text{ \AA}$) membranes. A 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 and/or organized within a phase) is the separation of the photogenerated products and the preclusion of the back reaction. Hopefully the reaction products can perform some useful function (e.g., create a voltage which drives other ions across a membrane; modify membrane transport properties; cause an electric current to flow through electrodes; lead to redox changes which produce pH changes or "energized" species (ATP)). A specific objective of these studies is the characterization of these processes: Are these reactions, for example, governed by the same factors controlling homogeneous chemical reactions? The role of diffusion in bringing reactants to a photoactivated surface will be studied theoretically and experimentally. Diffusion effects provide additional information for quantitating surface density of excited states and excited state products.

Publications

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Reports:

- BNL 26871 S. W. Feldberg, "An Electron Jump Model for Electron Translocation Across Lipid Bilayers," submitted for publication in Biophys. Journal.
- BNL 26935 Stephen W. Feldberg, Chi K. Chang, Ching-Bore Wang, and James A. Bell, "Electron Transport Across Glycero Monoolein Bilayer Lipid Membranes Facilitated by Magnesium Chlorins," submitted for publication in Biophys. Journal.
- BNL 26615 S. W. Feldberg, "Improvements on Computer Simulation of Electrochemical Phenomena Involving Hydrodynamics: The Rotating Disk and the Dropping Mercury Electrode," accepted for publication in Electroanalytical Chem.

Title: Metal Hydrides

FY 79: \$280,000

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

FY 80: \$277,000

Sponsor: Basic Energy
Sciences (DOE)

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. The difficulties which its storage presents 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. Such understanding is the long-range goal of this program. The experimental approaches through which it will be sought include the determination of pressure-temperature-composition relationships in selected metal-hydrogen systems, for the purpose of calculating thermodynamic properties; the establishment of crystal structures in metal-hydrogen systems, by means of x-ray and neutron diffraction; measurement of reaction rates in such systems; studies of surface structure and properties; and the influence of defects upon the behavior of intermetallic-hydrogen systems.

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 the development of correlations between isotopic differences in stability and other properties of alloy-hydrogen systems.

Publications

Journal Articles and Conference Proceedings:

F. Reidinger, J. J. Reilly, and R. W. Stoenner, "Single Crystal Preparation and Characterization of the Group VA Metal Hydrides and Deuterides," Journal of the Less-Common Metals 66, 23-32 (1979).

P. Thompson, J. J. Reilly, F. Reidinger, J. M. Hastings, and L. M. Corliss, "Neutron Diffraction Study of γ Iron Titanium Deuteride," J. Phys. F: Metal Physics 9, No. 4, 161-66 (1979).

James F. Lynch and John Tanaka, "The Dilute Solution of Hydrogen and Deuterium in β -Titanium," Scripta Metallurgica 13, 599-604 (1979).

S. M. Shapiro and F. Reidinger, "Neutron Scattering Studies of Superionic Conductors," in Topics in Current Physics, M. B. Salamon, editor, Springer-Verlag, Vol. 15, pp. 45-75 (1979).

R. J. Cava, F. Reidinger, and B. J. Wuensch, "Conductivity Mechanisms in The Superionic Phases of AgI and AgS as Determined by Neutron Diffraction," in Fast Ion Transport in Solids, P. Vashishta, J. N. Mundy, and G. K. Shenoy, editors, North Holland, pp. 217-20 (1979).

Reports:

- BNL 24693 R. J. Cava, F. Reidinger, and B. J. Wuensch, "Single Crystal Neutron-Diffraction Study of the Fast-Ion Conductor β -Ag₂S Between 186° and 325°C," accepted for publication in J. Solid State Chem.
- BNL 26899 P. Thompson, F. Reidinger, J. J. Reilly, L. M. Corliss, and J. M. Hastings, "Neutron Diffraction Study of α Iron Titanium Deuteride," accepted for publication in Journal of Physics F: Metal Physics.
- BNL 26047 J. J. Reilly, "Metal Hydride Technology," accepted for publication in Zeitschrift für Physikalische Chemie.
- BNL 25483^a J. F. Lynch, J. R. Johnson, and J. J. Reilly, "The Dilute Solution of Hydrogen and Deuterium in (C-15) TiCr_{1.8}," accepted for publication in Zeitschrift für Physikalische Chemie.
- BNL 25482^a R. J. Cava, F. Reidinger, and B. J. Wuensch, "A Single-Crystal Neutron-Diffraction Study of the Mobile Cu Ions in the Fast-Ion Conductor β -Cu₂S (High Chalcocite)," American Crystallographic Association Meeting, Honolulu, Hawaii, March 26-30, 1979.
- BNL 25397^a F. Reidinger, J. J. Reilly, and R. W. Stoenner, "A Single-Crystal Neutron Study of NbH 0.82 in the Superionic Phase," American Crystallographic Association Meeting, Honolulu, Hawaii, March 26-30, 1979.

^a Abstract

Title: High Temperature Chemistry

FY 79: \$238,000

Principal Investigator:
J. J. Egan

FY 80: \$195,000

Sponsor: Basic Energy
Sciences (DOE)

This task is a study of the thermodynamic and transport properties of inorganic substances at high temperatures and attempts to explain the results in terms of appropriate atomic models. The substances include solid and liquid compound semiconductors, solid electrolytes, and molten salts. Electrochemical techniques are used to investigate the effect of composition on the concentration, mobility, and diffusion of electrons and electron holes in these substances. Cells employing solid electrolytes at high temperatures as well as molten salt electrolytes prove especially useful for characterizing these systems. High temperature calorimetry is being used to study liquid semiconductors and other liquid alloy systems. Molten salts are studied since they are important for the development of high energy density batteries and fuel cells. The electronic conductivity of these melts in particular is examined by special techniques, since this property determines the self-discharge of batteries as well as the efficiency of electrolysis in the production of metals. Solid compound semiconductors of potential use as solar cells are studied by high temperature electrochemical techniques.

Publications

Journal Articles and Conference Proceedings:

J. Delcet, A. Brune, and J. J. Egan, "Coulometric Titrations Using CaF_2 and BaF_2 Solid Electrolytes to Study Alloy Phases," in Calculation of Phase Diagrams and Thermochemistry of Alloy Phases, Y. A. Chang and J. F. Smith, editors, The Metallurgical Society of AIME, pp. 275-86 (1979).

Reports:

- BNL 25520 J. Delcet and J. J. Egan, "The Free Energy of Formation of CaC_2 ," submitted for publication in J. Chem. Thermodynamics.
- BNL 25368 R. E. Davis, R. J. Heus, and J. J. Egan, "Electronic Conduction in Molten Potassium Chloride," submitted for publication in J. Electrochem. Soc.
- BNL 25661^a R. E. Davis, R. J. Heus, and J. J. Egan, "Electronic Conduction in Molten Sodium Chloride," 30th Meeting of International Society of Electrochemistry, Trondheim, Norway, Aug. 27-31, 1979.
- BNL 26996 R. E. Davis and J. J. Egan, "Electronic Properties of the Semiconductor $\text{Li}_{3+\delta}\text{Sb}$ at 355°C ," Spring Meeting of the Electrochemical Society, St. Louis, Missouri, May 11-16, 1980; submitted for publication in the Journal of the Electrochemical Society.
- BNL 23809 J. Delcet and J. J. Egan, "Thermodynamics of Some Dilute Binary and Ternary Ca Alloys," submitted for publication in Metallurgical Trans. B.
- H. Pfeiffer, R. J. Heus, and J. J. Egan, "Thermodynamics and Electrical Conductance of Liquid Na_3Bi ," presented at Gordon Conference on Molten Salts and Metals, Wolfeboro, New Hampshire, Aug. 20-24, 1979.

^a Abstract

Title: Chemistry and Physics of Coal Utilization

FY 79: \$102,000

Principal Investigator:
T. E. Gangwer

FY 80: \$105,000

Sponsor: Basic Energy
Sciences (DOE)

The broad scope of this research is to contribute to the understanding of hydrogenation/dehydrogenation chemistry relevant to coal conversion. A central objective of the study is the development of basic kinetic data and reaction pathway mechanisms for hydrogenation reactions generally applicable to a broad range of conversion processes. The current focus of this task is to develop basic mechanistic information on the hydrogenation reactions that occur in organic hydrogen donor systems. The detailed reaction mechanisms are determined for these hydrogen transfer systems. The work is currently aimed at gaining kinetic and mechanistic insight into this complex organic chemistry by developing a sound understanding of the hydroaromatic donor solvent reactions. The nature of the chemistry occurring at phase interfaces (gas/solid/liquid) is being studied. The hydrogen transfer from organic donor solvents to model compounds is being studied to determine the detailed mechanistic pathways that give rise to the products. The insight gained from this effort will contribute to the understanding of liquefaction hydrogenation processes and product formation.

Publications

Journal Articles and Conference Proceedings:

T. Gangwer, "Gas Phase UV-V Spectra of Reacting Hydroaromatics Systems," J. Phys. Chem. 83, 2176-78 (1979).

T. Gangwer, D. MacKenzie, and E. Casano, "Hydroaromatic Hydrogenation/Dehydrogenation," J. Phys. Chem. 83, 2013-15 (1979).

T. Gangwer and H. Prasad, "Hydrogen Transfer Catalytic Activity of Minerals Common to Coal," Fuel 58, 577-84 (Aug. 1979).

Reports:

- BNL 25911^a T. Gangwer, "Hydrogen Transfer Catalytic Activity of Minerals Common to Coal," 13th Middle Atlantic Regional Meeting, West Long Branch, New Jersey, March 19-23, 1979.
- BNL 26304^a T. Gangwer, "Donor Solvent Kinetics and Coal Liquefaction Modeling," Materials Research Society Meeting, Cambridge, Mass., Nov. 26-30, 1979.
- BNL 26347^a T. Gangwer, "The Mechanism of Tetralin Dehydrogenation in the Presence of Iron Catalysts," 31st Southeast Regional Meeting of the American Chemical Society, Roanoke, Virginia, Oct. 24-26, 1979.
- BNL 26088^a T. Gangwer, "Hydroaromatic Kinetics Monitored Using UV-V Spectroscopy," Pacific Conference on Chemistry and Spectroscopy of the American Chemical Society, Pasadena, California, Oct. 10-12, 1979.
- BNL 26434 T. Gangwer, "Transfer of Hydrogen by Hydroaromatics. I. The Mechanism of Tetralin Dehydrogenation in the Presence of Iron Catalysts," submitted for publication in J. Phys. Chem.

^a Abstract

Title: An Investigation of Carbon Oxide Reactions

FY 79: \$65,000

Principal Investigator:
R. Sapienza

FY 80: \$103,000

Sponsor: Basic Energy
Sciences (DOE)

This task is an experimental investigation of the mechanism(s) of carbon oxide reduction reactions, principally on metal and metal oxide surfaces, where appropriate homogeneous analogs are included. Preliminary review of the literature, plus some experimental results previously obtained here, indicates that, with two reasonable assumptions, much experimental data uncovered so far--end product distributions, observed intermediates, relative catalytic activities, suspected "poisoning"--can be understood.

The elements of the task are designed to: (1) investigate and demonstrate the range of validity of the postulates; (2) specify the chemical, thermodynamic, and structural parameters of importance; and (3) develop a theory with predictive capability for these important classes of reactions.

Publications

Journal Articles and Conference Proceedings;

R. S. Sapienza, M. J. Sansone, L. D. Spaulding, and J. F. Lynch, "Novel Interpretations of Carbon Oxide Reductions," in Fundamental Research in Homogeneous Catalysis, M. Tsutsu, editor, Plenum Publishing Corp., Vol. 3, 179 (1979).

Title: Cyclic Separations Process Research

FY 79: \$141,000

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

FY 80: \$145,000

Sponsor: Basic Energy
Sciences (DOE)

This program consists of a study of the application of cyclic separation processes to separation problems arising in energy technology. The purposes of the program are two-fold: to obtain an understanding of the characteristics and basis of operation of cyclic separation processes as a class, and to explore the feasibility of using these processes to perform specific separations of interest in the energy field.

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

Elements of the program include development of the theory of cyclic processes, measurements of equilibrium and kinetic properties of selected fluid-solid separation systems, measurement of the characteristics of cyclic separation processes employing these systems, 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.

Publications

Journal Articles and Conference Proceedings:

Y. W. Wong and F. B. Hill, "Equilibrium and Kinetics Studies of Hydrogen Isotope Exchange on Vanadium Hydride," AIChE Journal 25, No. 4, 592-99 (1979).

Reports:

- BNL 26346^a Frank B. Hill, "Separation of Hydrogen Isotopes Via Chromatographic Processes Using a Metal Hydride," Gordon Research Conference on Separation and Purification, New London, New Hampshire, Aug. 13-17, 1979.
- BNL 26215^a Y. W. Wong, F. B. Hill, and Y. N. I. Chan, "Studies of the Separation of Hydrogen Isotopes by a Pressure Swing Adsorption Process," Symposium on Separation Science and Technology for Energy Applications, Gatlinburg, Tenn., Oct. 30 - Nov. 2, 1979; submitted for publication in Journal of Separation Science and Technology.
- BNL 25662^a Y. W. Wong, Y. N. I. Chan, and F. B. Hill, "Separation of Hydrogen Isotopes Via Pressure and Temperature Swing Processes," AIChE Meeting, San Francisco, California, Nov. 25-29, 1979.
- BNL 26663^a Y. W. Wong, Y. N. I. Chan, and F. B. Hill, "Studies of Hydrogen Isotope Separation Using Vanadium Hydride in a Temperature Cycling Process," 72nd AIChE Annual Meeting, San Francisco, California, Nov. 25-29, 1979.
- BNL 26664 Yau Nam I. Chan, Frank B. Hill, and Yiu Wah Wong, "Equilibrium Theory of a Pressure Swing Adsorption Process," submitted for publication in Journal of Chemical Engineering Science.

^a Abstract

Title: Trace Element Analysis Using Synchrotron Radiation

FY 79: \$47,000

Principal Investigator:
B. M. Gordon

FY 80: \$45,000

Sponsor: Basic Energy
Sciences (DOE)

This program is concerned with the application of the National Synchrotron Light Source (NSLS) to multielemental trace analysis. The construction of an electron synchrotron storage ring dedicated to the use of x rays makes possible a program of trace element analysis by x-ray fluorescence techniques with special emphasis on the use of a scanning x-ray microprobe with one micrometer spatial resolution. The properties of synchrotron radiation, including polarization, high brightness, and tuneability over a wide energy range, lead to sensitivities much greater than those for microprobes using protons or electrons. This program is developing the optimum conditions necessary to provide the greatest sensitivity for the technique consistent with its application to a variety of fields, including the geosciences, life sciences, material sciences, and atmospheric sciences. Most important is the development of an optics system to provide for the greatest demagnification and highest sensitivity. Emphasis is also to be placed on the development of a bulk analysis system with minimum detectable levels in the 50 ppb range in thin dry samples. In addition, synchrotron radiation provides the opportunity to do chemical speciation of a trace element at the ppm level by determination of the absorption edge energy and subsequent comparison with edge energies of known model compounds of that element.

Publications

Reports:

BNL 25262^a B. M. Gordon, "Trace Element Analysis By Synchrotron Radiation Induced X-Ray Fluorescence," 2nd Conference on Inorganic and Nutritional Aspects of Cancer, La Jolla, California, Jan. 3-5, 1979.

^a Abstract

Barry Gordon, "Measurement of Trace Element Concentrations in Tissue: X-Ray Fluorescence Using Synchrotron Radiation and Proton Microprobes," presented at Gordon Research Conference on Magnesium in Biochemical Processes and Medicine, Plymouth, New Hampshire, August 6-10, 1979.

Title: Determining Fragile Molecules in the Environment*

FY 79: \$110,000

Principal Investigators:
L. Newman, R. Tanner

FY 80: \$100,000

Sponsor: Basic Energy
Sciences (DOE)

*This work is being conducted in the Environmental Chemistry Division and is described in "Program Summaries for 1979 - Environmental Sciences Programs," BNL 51169.

Title: Specific Molecular Property Detectors for Chromatographic Analysis*

FY 79: -

Principal Investigators:
J. Gaffney, E. Premuzic

FY 80: \$45,000

Sponsor: Basic Energy
Sciences (DOE)

*This work is being conducted in the Environmental Chemistry Division and is described in "Program Summaries for 1979 - Environmental Sciences Programs," BNL 51169.

Title: The Rotating Fluidized Bed Combustor^{*}

FY 79: \$25,000

Principal Investigator:
F. B. Hill

FY 80: -

Sponsor: Basic Energy
Sciences (DOE)

This task consists of a study of the rotating fluidized bed as a chemical reactor for the conduct of fast reactions such as combustion. 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. Restraint of the particles by this force is the distinctive feature of this system and leads to high gas capacity and exceptional resistance to elutriation, and therefore suitability for the conduct of fast reactions.

The program consists of experimental and theoretical studies of the fluid dynamics and reaction properties of the rotating fluidized bed. Measurements are being made of the properties of gas bubbles in rotating liquids and in rotating gas-solid fluidized beds. These will be followed by measurements of the exchange between bubbles and the emulsion phase and by studies of the chemical reaction properties of the rotating system using a well characterized model fast reaction. A parallel theoretical effort on the influence of rotation on fluidization is underway.

The results of the program may be of interest in connection with the combustion of various kinds of fuels.

Publications

Reports:

BNL 50990 Robert Pfeffer and Frank B. Hill, "A Feasibility Study on the Use of a Rotating Fluidized Bed as a Dust Filter," March 1979.

^{*}This program was terminated as of 9/30/79.

Title: Two-Phase Flow Studies*

FY 79: -

Principal Investigator:
O. C. Jones

FY 80: \$50,000

Sponsor: Basic Energy
Sciences (DOE)

The efforts in this task are directed towards two major goals: (a) the development of a simple, low cost, and objective method for flow pattern recognition in two phase gas-liquid flows, and (b) the measurement of turbulent characteristics in both phases to study the connection between turbulence and phase distributions, which in turn is expected to lead to the development of models for the analytical prediction of the transition between the four major flow regimes of bubbly, slug, annular, and annular-mist flows. Statistical analysis of pressure differentials and dynamic pressure fluctuations will be used to develop the flow pattern recognition technique. Light scattering at the gas-liquid interface is another property that will be explored towards the same goal. Laser Doppler Velocimetry and Hot-film Anemometry will be utilized for turbulence measurements. To prevent distortion, and hence signal loss, of laser beams special micro-optic and/or fiber optic probes may be developed to guide the laser beams. Similarly, special split film sensors would be designed to enable measurements in both phases to be made.

Publications

None. This is a new program.

*This work is being conducted in the Department of Nuclear Energy.

Title: Pre-College Teacher Development in Science - Institute on Energy

FY 79: \$18,700

Principal Investigator:
D. J. Metz

FY 80: \$19,684

Sponsor: National Science
Foundation

The objectives of this activity are, in general, to intensify and expand the level of interaction between the local secondary 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.

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 thirty sessions are subdivided into three time 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 to

1. make an oral presentation,
2. write a report,
3. develop an individual project.

Publications

None.

PLANS FOR 1980

Most of the research programs in this area are relatively long-range basic research efforts in which significant changes in direction or level of effort evolve over a period of time that is generally longer than a year. In that sense, the plans for 1980 are predominantly logical continuations of efforts initiated in 1979, or even earlier.

In Photochemistry, a vigorous effort in pursuing phenomena associated with photoenergy transduction will be maintained, including a further development of porphyrin mediated processes, the photophysics and photochemistry of adsorbed species, and electron transport across membranes. In Chemical Physics, the study of the kinetics and mechanisms of specific atom-molecule and radical-molecule reactions associated with the combustion of alternative fuels will continue, using available instrumentation and techniques and developing additional experimental techniques that will capitalize on the future availability of the NSLS.

In Chemical Energy, further exploration of the relationship between structure and thermodynamics of metal-hydrogen systems will be pursued. The study of the kinetics and mechanisms of several classes of processes important to coal liquefaction (hydrogen donor solvents) and coal conversion (carbon oxide reductions) will continue. The high temperature electrochemistry study will continue to investigate the thermodynamic and transport properties of compound semiconductors and will begin to explore the application of its electrochemical techniques to an investigation of gas-solid reactions.

In Separations, emphasis will continue on the investigation of various cyclic separations processes in hydrogen isotope separation, gas stream purification (e.g., helium removal from natural gas), and, in the near future, rare earth separations (related to nuclear waste management).

In Analysis, the program to develop trace multi-element analysis using NSLS X-rays will continue, as will the two other analytical programs conducted in the Environmental Chemistry Division.

Finally, in Chemical Engineering Sciences, a new program in two phase flow is being initiated, with the work being performed in the Department of Nuclear Energy.

METALLURGY AND MATERIALS SCIENCE DIVISION

Masaki Suenaga

At present the major efforts in this Division are the investigation of properties of superconducting Al₅ compounds, amorphous semiconductors for solar cells, and metallurgical properties of metals and alloys with dissolved hydrogen. Primary emphasis in these programs is on gaining a fundamental understanding of the microscopic and microstructural factors influencing the properties of the materials. Development of high efficiency solar cells, superconductors with higher mechanical tolerance and with low loss ac losses, and the selection of dielectric tapes for electrical power transmission lines are also carried out in collaboration with applied programs. The Division is also responsible for providing metallurgical services such as metallography and mechanical testing to other parts of the Laboratory.

In performing this research and development advantage is taken whenever possible of special facilities available at BNL; the use of 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 with synchrotron radiation will be emphasized as required by the programs described above.

SIGNIFICANT ACCOMPLISHMENTS

The detailed technical progress in 1979 of each program is fully described in budget submission documents and published reports. The purpose of this section is to focus attention on two examples of selected accomplishments that are considered to be more significant, at this writing, than many others.

Kinetics of Hydrogen Dissolution in Transition Metals

Significant progress was made this year in understanding what factors govern the rate at which hydrogen moves between the gas phase and solution in transition metals such as Nb and Ta. Such knowledge is needed as a basis for improving the kinetics of hydrogen charging and removal in metal hydrogen storage systems.

This progress in understanding was a consequence of experiments by M. A. Pick et al. of the Metallurgy and Materials Science Division in collaboration with M. Strongin et al. of the Physics Department. These experiments employed the tools of modern surface science, such as ultrahigh vacuum conditions, Auger electron spectroscopy, low-energy electron diffraction, etc., to provide well-characterized surfaces of highly pure Nb and Ta foils, to which thin metallic overlayers could be added if desired. Hydrogen uptake and emission rates were then measured as a function of temperature and hydrogen pressure. It was found that the uptake rates can be significantly enhanced or decreased by the surface deposition of a thin layer of Pd, Pt, or Ni. The hydrogen uptake rates, e.g., sticking coefficients, were measured as a function of the overlayer thickness. In the case of Pd it was found that a layer less than one monolayer thick will either not change or even inhibit the hydrogen uptake, whereas a layer over one monolayer thick will enhance the sticking coefficient to a value of 1. It was found that the change at one monolayer is related to a phase transition of the Pd surface layer at that coverage. In this structural change of the overlayer, the Pd goes from a commensurate structure on (110) Nb and Ta to (111) fcc Pd for thicker layers. Both Pt and Ni do not exhibit this effect but do increase the uptake rate by an amount depending on their thickness. Thick overlayers inhibit uptake due to a limited permeation rate through the layer.

The measurements led to a theoretical model for the absorption and desorption kinetics of hydrogen by metals such as niobium. The kinetics are governed by the existence of a strongly bound chemisorbed hydrogen state at the surface. The energy of this surface state is lower than that in the bulk (chemisorption energy > solution energy) leading to a surface concentration larger than the bulk concentration. The model includes the processes of hydrogen impingement on the surface and subsequent dissociation, as well as the reverse process, and transitions of hydrogen between the bulk and chemisorbed phases. The dominating factor is the existence of a surface barrier which depends on the chemisorption energy. The surface barrier model for hydrogen uptake was used to derive an expression for the sticking coefficient of H on Nb. This expression explains some of the hitherto unexplained features of previous measurements in the pressure, temperature, and coverage dependence of the sticking coefficient of H on Nb, and furthermore allows one to extract the chemisorption energy from the data. The expression can be generalized to other metal-gas systems in which solution plays a major role

Solar Materials

The Solar Materials Program is pursuing research on amorphous semiconductor materials with two aspects in mind: i) a basic understanding of the materials ("Basic Processes and Microstructural Properties of Amorphous Semiconductors"), and ii) a focus toward photovoltaic conversion ("Advanced Amorphous Materials for Photovoltaic conversion"). In the past year, significant technical accomplishments include the following features of materials growth and characterization:

1. For plasma-deposited "a-Si:H" materials, we demonstrated the chemical modification of optoelectronic behavior via the incorporation of common atmospheric impurities (nitrogen and oxygen, i.e., air). The importance of this work lies in the evolving definition of what is the nominally intrinsic silicon-hydrogen amorphous alloy a-Si:H -- as a basis for tailoring optoelectronic quality. As this work progresses, we find that the more correct designation for the usual a-Si:H alloy should perhaps be a-Si:(H,O,N,C,...). The implication is that the optoelectronic properties of plasma-deposited

"a-Si:H" alloys reflect varying degrees of incorporated atmospheric impurities.

- a) For the first time, low impurity films were shown to have anomalous photoconductive behavior as a function of temperature and illumination in which thermal and infrared quenching effects, and supralinearity are all observed.
 - b) Tailoring the degree and kind of impurity incorporation has given rise to some of the most photoconductive films ever produced (photoconductivity $\sigma_p > 10^{-4} (\Omega \cdot \text{cm})^{-1}$ at a flux of $10^{14} \gamma/\text{s cm}^{-2}$). Synergistic effects of oxygen and nitrogen produce classic photoconductive behavior in these films. Such films exhibit electronic doping by nitrogen.
 - c) Preliminary results show interesting correlations with photovoltaic conversion efficiencies.
2. For the first time, the technique of optical emission spectroscopy was used to study plasma deposition of a-Si:H materials. (In plasma etching of photoresists, etc., this technique was used for several years.) Optical emission spectroscopy is one method (to be complemented by others that we shall utilize) that can lead to control of plasma processing, a feature of considerable commercial significance.
- a) Emitting reactive species such as SiH, Si, SiH⁺, H, and H₂ were identified and monitored during plasma deposition.
 - b) Important impurities such as N₂, SiO, and SiCl were detected in the plasma, and in some cases, their concentration was calibrated by this diagnostic means. The presence of N₂ and SiO was directly correlated with altered film properties (such as dark conductivity and photoconductivity, and possibly microstructure). The presence of the SiCl bond owes its origin to unwanted chlorosilane impurities in silane tanks.
3. Measurements of microstructure using STEM, SEM, and electron microprobe techniques were carried out on a-Si:H materials.

- a) High resolution STEM images ($\sim 2\text{\AA}$ resolution) exhibit the presence of density fluctuations on a scale of $\sim 10\text{\AA}$ for ultra-thin films ($\sim 100\text{\AA}$ thick). Correlations were observed with the atmospheric impurity content of the plasma-deposited films. Further studies are progressing in order to separate out substrate effects.
 - b) SEM micrographs of fracture surfaces revealed no columnar structure in any of our materials. The lack of this feature may be correlated with "good" optoelectronic properties. SEM was also used to detect the presence of spallation fragments in some of our plasma-deposited materials. In this regard, SEM was a useful diagnostic technique.
4. Infrared transmission studies were initiated of vibrational modes characteristic of bonding in a-Si:H materials. Oxygenated materials exhibited: i) the Si-O-Si antisymmetric stretching mode (at $\sim 980\text{ cm}^{-1}$), and ii) the "induction effect" in which the monohydride stretch mode $\equiv \text{Si-H}$ at 2000 cm^{-1} shifts to $\sim 2100\text{ cm}^{-1}$ owing to the backbonding of oxygen in the configuration =Si-H . Concentrations of bonded oxygen were estimated from the infrared data by calibration with secondary ion mass spectroscopy (SIMS) measurements. Highly oxygenated a-Si:(H,O) materials were produced that behave as dielectrics ([O] $\sim 40\%$).
 5. Spectral- and temperature-dependent measurements of photoluminescence in a-Si:H alloys demonstrated efficient low-temperature radiative recombination that peaks at 1.3 eV. Films electronically doped by nitrogen exhibit a low-energy peak at $\sim 0.95\text{ eV}$ that may be associated with a nitrogen-activated defect in the alloy.

Title: Relationships Between
Properties and Structures

FY 79: \$ 530,000

Principal Investigators:

D. O. Welch

M. Suenaga

C. S. Pande

FY 80: \$ 250,000

Sponsor: Basic Energy
Sciences (DOE)

It is the task of this program to study the basic relationship between microscopic structure and macroscopic properties, emphasizing studies of superconducting materials with high critical temperatures and high critical magnetic fields. Particular stress is placed upon studies of superconducting compounds with the A15 crystal structure, such as Nb₃Sn, V₃Ga, etc., although compounds with other structures, such as Laves and Chevrel phases, are also of interest. The research includes investigations of the basic physical properties of superconducting compounds and of 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 the techniques for producing new superconducting materials, ranging from explosive formation of Nb₃Si to methods for producing multifilamentary conductors utilizing compounds with high critical temperature and magnetic field other than Nb₃Sn and V₃Ga. It is the objective of this research to provide the basic data and understanding of the fundamental physical metallurgy of superconducting materials required for their effective practical utilization.

Publications

Journal Articles and Conference Proceedings:

D. Dew-Hughes and V. D. Linse, "The Formation of Nb_3Si by Explosive Compression," J. Appl. Phys. **50**, 3500 (1979).

D. Dew-Hughes, "The Properties of Superconducting Nb_3Si ," IEEE Trans. on Magnetism **MAG-15**, 490 (1979).

T. Luhman, M. Suenaga, D. O. Welch, and K. Kaiho, "Degradation Mechanism of Nb_3Sn Composite Wires Under Tensile Strain at 4.2 K," IEEE Trans. on Magnetism **MAG-15**, 699-702 (1979).

C. S. Pande, "Electron Microscopy of Neutron Irradiated Nb_3Sn ," Phys. Stat. Sol. (a) **52**, 687 (1979).

Reports:

BNL 25370^a J. F. Bussiere, D. O. Welch, and M. Suenaga, "A Measurement of the Temperature Dependent Young's Modulus of Polycrystalline Nb_3Sn ," 1979 March Meeting of the Am. Phys. Soc., Chicago, IL, March 19-23, 1979; Bull. Am. Phys. Soc. **24**, 425 (1979).

BNL 25365^a D. O. Welch, O. W. Lazareth, G. J. Dienes, and R. D. Hatcher, "Shell Model Calculation of the Ionization Potentials of Alkali Halides," 1979 March Meeting of the American Phys. Soc., Chicago, IL, March 19-23, 1979; Bull. Am. Phys. Soc. **24**, 404 (1979).

BNL 25362^a K. Aihara, D. O. Welch, M. Suenaga, and T. S. Luhman, "Alteration by Elastic Strain of the Superconducting Transition Temperature of Nb_3Sn , V_3Ge , V_3Ga , and V_3Si in 'Bronze-Process' Composite Wires," 1979 March Meeting of the American Phys. Soc., Chicago, IL, March 19-23, 1979; Bull. Am. Phys. Soc. **24**, 456 (1979).

BNL 24978^a J. F. Bussiere, D. O. Welch, and M. Suenaga, "Elastic Modulus of Polycrystalline Nb_3Sn Between 4.2 and 300 K," AIME Annual Meeting, New Orleans, LA, February 1979.

BNL 27042^a D. O. Welch, O. W. Lazareth, G. J. Dienes, and R. D. Hatcher, "A Theoretical Study of Interatomic Forces and Point Defects in A15 Structure Superconductors," Fall Meeting of AIME, Milwaukee, WI, Sept. 17-20, 1979.

^a Abstract

- BNL 26496^a J. F. Bussiere, D. O. Welch, and M. Suenaga, "Young's Modulus of Polycrystalline Nb₃Sn between 4.2 and 300 K," accepted for publication in J. Appl. Phys.
- BNL 26391^a M. Suenaga, K. Aihara, K. Kaiho, and T. Luhman, "Superconducting Properties of (Nb,Ta)₃Sn Wires Fabricated by the Bronze Process," accepted for publication in Adv. in Cryogenic Eng. 26.
- BNL 25949 D. O. Welch, J. F. Bussiere, and M. Suenaga, "Softening of Young's Modulus of Polycrystalline Nb₃Sn," International Conf. on Martensitic Transformations (ICOMAT-79), Cambridge, MA, June 24-29, 1979.
- BNL 26576 D. Dew-Hughes, "The Effect of Carbon on the Superconductivity of V₃Si," accepted for publication in Physica Status Solidi (a).
- BNL 26753 D. Dew-Hughes and R. Jones, "The Effect of Neutron Irradiation Upon the Superconducting Critical Temperature of Some Transition Metal Carbides, Nitrides, and Carbonitrides," accepted for publication in Appl. Phys. Letts.
- BNL 25711 D. Dew-Hughes, R. Caton, R. Jones, and D. O. Welch, "Recovery by Annealing of T_c in Disordered Nb₃Pt," accepted for publication in Proceedings of the 3rd Conf. on Superconductivity in d- and f-Band Metals, San Diego, CA, 1979.
- BNL 26771 D. Dew-Hughes, "Reordering Kinetics of Disordered Al₅ Compounds," accepted for publication in J. Phys. Chem. Solids.
- BNL 26430 K. G. Lynn and D. O. Welch, "Slow Positron Studies of Metal Single Crystals: I. Positronium Formation at Ag(100), Ag(111), and Cu(111) Surfaces," accepted for publication in Phys. Rev.
- BNL 25769 C. S. Pande, "Direct Observation of Defects in Al₅ Compounds Produced by Fast-Neutron Irradiation," accepted for publication in Proc. of the 3rd Conf. on Superconductivity in d- and f-Band Metals, San Diego, CA, 1979.
- BNL 26400 D. O. Welch, "Alteration of the Superconducting Properties of Al₅ Compounds and Elementary Composite Superconductors by Nonhydrostatic Elastic Strain," accepted for publication in Adv. in Cryogenic Engr. 26.
- BNL 26407 T. Luhman and D. O. Welch, "An Analysis of Critical Current-Bend Strain Relationships in Composite Nb₃Sn Superconducting Wires," 8th Symposium on Engineering Problems of Fusion Research, San Francisco, CA, Nov. 12-16, 1979.

^aAbstract

D. Dew-Hughes, "Introduction to Superconducting Materials," Treatise on Materials Science and Technology 14: Metallurgy of Superconducting Materials, T. Luhman and D. Dew-Hughes, eds., 1-46, Academic Press, NY, 1979.

D. Dew-Hughes, "Physical Metallurgy of Al₅ Metallurgy of Al₅ Compounds," Treatise on Materials Science and Technology 14: Metallurgy of Superconducting Materials, T. Luhman and D. Dew-Hughes, eds., 137-170, Academic Press, NY, 1979.

C. S. Pande, "Superconductivity and Electron Microscopy," Treatise on Materials Science and Technology 14: Metallurgy of Superconducting Materials, T. Luhman and D. Dew-Hughes, eds., 171-220, Academic Press, NY, 1979.

D. Dew-Hughes and T. Luhman, "Future Materials Development," Treatise on Materials Science and Technology 14: Metallurgy of Superconducting Materials, T. Luhman and D. Dew-Hughes, eds., 427-446, Academic Press, NY, 1979.

M. Suenaga, K. Aihara, and W. Marancik, "Superconducting Properties of Multifilamentary Nb₃Sn Wires by a Wrap Process," AIME Fall Meeting, Milwaukee, WI, September 17-20, 1979.

D. O. Welch and D. J. Metz, "Technology Crosscut Review of Basic Research Related to the Technologies of Energy Conversion, Transmission, and Storage," accepted for publication in Office of Basic Energy Sciences Report on Technology Crosscut Reviews of Basic Research.

Title: Radiation Damage

FY 79 \$210,000

Principal Investigator:
C. L. Snead, Jr.

FY 80 \$230,000

Sponsor: Basic Energy
Sciences (DOE)

The purposes of this program are twofold: (1) to investigate the effects of lattice defects on the electrical and mechanical properties of materials, and (2) utilize observed property changes to obtain a better understanding of the nature of radiation damage induced by differing types of irradiation. The emphasis lies in the first category where the critical properties of type-II superconductors are investigated as a function of several types of irradiation damage. This provides information on the expected response of high-field magnets to be operated in radiation environments: e.g., ISABELLE and fusion-reactor magnets. These studies utilize various radiation-damage sources to provide controlled sources of defects in superconductors so that the physical mechanisms coupling defects to critical-properties changes can be elucidated. This latter information also is useful in objective (2) where the comparison of property changes due to differing types of particle damage bears on the determination of the nature of the damage created by each. The determination of the defect state in mainly high-energy-proton and neutron-irradiated specimens in this category are achieved by relating the above measurements to others such as microhardness and electron microscopy, and to damage-energy analyses. Other measurements such as 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.

Publications

Journal Articles and Conference Proceedings:

K. G. Lynn, C. L. Snead, Jr., J. J. Hurst, and K. Farrell, "Determination of the Vacancy Formation Enthalpy for High Purity Ni," Proc. Intern. Conf. Positron Annihilation, Lake Yamanaka, Japan, R. R. Hasiguti and K. Fujiwara, eds., 119-124, The Japan Institute of Metals, Sendai, Japan, 1979.

C. L. Snead, Jr., A. N. Goland, K. G. Lynn, Y. Platov, and M. Guinan, "Positron Trapping by Defects in Pt, Al, and Al-0.1-at.% Mg Following d-Be Neutron Irradiation," Proc. Intern. Conf. Positron Annihilation, Lake Yamanaka, Japan, R. R. Hasiguti and K. Fujiwara, 725-730, The Japan Institute of Metals, Sendai, Japan, 1979.

Reports:

BNL 26876 C. L. Snead, Jr. and M. Suenaga, "Radiation-Enhanced-Diffusion Growth of Nb₃Sn Monofilaments: Grain-Size Effects on Critical-Current Density," accepted for publication in Appl. Phys. Letters.

BNL 26679 C. L. Snead, Jr., A. N. Goland, K. G. Lynn, Y. Platov, and M. Guinan, "Investigation of Damage in Pt, Al, and Al-0.1-at.% Mg Produced by d-Be and Fission-Reactor Neutrons using Positron Annihilation," accepted for publication in J. Nucl. Mat.

BNL 26514R K. G. Lynn, C. L. Snead, Jr., and J. J. Hurst, "Positron Lifetime Studies of Pure Ni from 4.2 to 1700 K, accepted for publication in J. of Physics F: Metal Physics.

BNL 26656 P. J. Schultz, K. G. Lynn, I. K. MacKenzie, Y. C. Jean, and C. L. Snead, Jr., "Temperature Dependence of the Positron-Annihilation Characteristics in Molybdenum Containing Voids, accepted for publication in Phys. Rev.

BNL 27178 R. Caton, Sigurts Araj, C. A. Moyer, M. Z. El-Gamal, and C. L. Snead, Jr., "Crystallization Neutron Irradiation and Annealing in Glassy Ti₅₀-Be₄₀-Zr₁₀," accepted for publication in J. of Non-crystalline Solids.

A. R. Sweedler, C. L. Snead, Jr., and D. E. Cox, "Irradiation Effects in Superconducting Materials," Treatise on Materials Science and Technology 14 Metallurgy of Superconducting Materials, T. Luhman and D. Dew-Hughes, eds., 349-426, Academic Press, NY, 1979.

C. L. Snead, Jr., "INTOR-Data-Base Assessment: Radiation Effects in Materials of Superconducting Magnets," Excerpted in U.S. Contribution to the International Tokamak Reactor Workshop. June 1979.

R-Revised

Title: Fabrication and Properties of
Conductors for MFE Magnets

FY 79: \$200,000

Principal Investigator:
T. S. Luhman

FY 80: \$180,000

Sponsor: Magnet Fusion
Energy (DOE)

This program is concerned with the mechanical and metallurgical aspects of the design, fabrication, and utilization of superconducting composite conductors in fusion magnet systems. Particular emphasis is given to understanding and improving the mechanical and high-field superconducting properties of Al5 diffusion-processed conductors. Experimental determinations of superconducting properties form the basis of our 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 properly assessed, 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.

To insure utility of this work an active communication is maintained with the magnetic fusion community, especially the groups at Lawrence Livermore Laboratory (LLL) and Oak Ridge National Laboratory (ORNL).

Publications

Journal Articles and Conference Proceedings:

T. Luhman, "Effects of Be Alloy Additions to the Bronze Matrix of Nb₃Sn Monofilamentary Wires," J. Appl. Phys. 50, 3766 (1979).

Reports:

- BNL 26407 T. Luhman and D. O. Welch, "An Analysis of Critical Current-Bend Strain Relationships in Composite Nb₃Sn Superconducting Wires," Proc. of the 8th Symposium on Engr. Problems of Fusion Research, San Francisco, CA, November 13-16, 1979.
- BNL 26950 K. Aihara, M. Suenaga, and T. Luhman, "Effects of Differential Thermal Contraction Between the Matrix and the Filaments in Mono- and Multifilamentary Nb₃Sn on the Superconducting Critical Temperature," Proc. of the 8th Symposium on Engr. Problems of Fusion Research, San Francisco, CA, November 13-16, 1979.
- BNL 26450 T. Luhman, K. Kaiho, and M. Suenaga, "Effects of Alloying on the Strain Response of Critical Currents in Nb₃Sn Conductors," accepted for publication in Advances in Cryogenic Eng.
- BNL 26480 K. Kaiho, T. Luhman, M. Suenaga, and W. B. Sampson, "Effects of Bending on the Superconducting Critical Current Density of Monofilamentary Nb₃Sn Wires," accepted for publication in Appl. Phys. Letters.
- BNL 26025^a T. Luhman, "Mechanical Behavior and Stress Effects in Composite Nb₃Sn Superconductors," Invited talk presented at TMS-AIME Fall Meeting, Milwaukee, WI, September 1979.

^a Abstract

Title: Superconducting Power Transmission Lines*

FY 79: ~\$400,000

Principal Investigator:
C. Klamut, A. Muller, M. Suenaga

FY 80: ~\$400,000

Sponsor: Electric Energy
Systems (DOE)

This study includes the investigation of fabrication processes for superconducting tapes suitable for ac (60 Hz) applications, of mechanisms for ac losses in Al₅ compounds, of relationship between microstructures to the 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 major effort of the dielectric tape development program is an investigation of dielectric materials to provide tapes that are electrically, mechanically, and thermally suitable for use as insulation on ac superconducting and oil filled cables. Also being developed and applied is a radiographic technique to study tape-lapping patterns and to locate mechanical defects in existing cables. Measurements of mechanical (strength, friction, etc.) and thermal (expansion coefficients) properties of these tapes are made at room as well as liquid helium temperatures.

Publications

Journal Articles and Conference Proceedings:

E. D. Forsyth, A. J. McNerney, A. C. Muller, "Performance of Synthetic Materials in the Lapped Insulation of Cryogenic and Ambient Temperature Cables", Presented at the IEEE/PES Conference and Exposition on Overhead and Underground Transmission and Distribution, IEEE Pub. No. 79CH1399-5-PWR, Atlanta, Georgia, Apr. 1-6, 1979.

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

E. B. Forsyth, A. J. McNerney, A. C. Muller, "The Development of Synthetic Insulating Tape for EHV Cables," Proceedings of the Second IEE International Conference on Progress in Cables and Overhead Lines for 220 kV and Above, London, England, Sept. 4-6, 1979.

A. C. Muller, "X-Ray Examination of Insulation in Lapped High Voltage Underground Power Transmission Cables," Proceedings of the National Fall Conference of the American Society for Nondestructive Testing, St. Louis, Missouri, Oct. 15-18, 1979.

A. C. Muller, "X-Ray Examination of Lapped Electrical Insulation," Proceedings of 1979 Conference on Electrical Insulation and Dielectric Phenomena, Whitehaven, Pennsylvania, Oct. 21-25, 1979.

Title: Physical Metallurgy of Metal-Hydrogen Systems

FY 79: \$ 150,000

Principal Investigators:

M. A. Pick
D. O. Welch
C. S. Pande

FY 80: \$ 400,000

Sponsor: Basic Energy
Sciences (DOE)

The purpose of this research is to obtain a fundamental understanding of the metallurgical factors which influence the behavior of hydrogen in selected metal systems. Of particular interest are the roles of microstructure, lattice defects, alloying effects, and surface properties in the thermodynamics, kinetics, and mechanisms of hydrogen uptake and release in transition metals, solid solutions, and intermetallic compounds. The effect of dissolved hydrogen upon fracture strength is also of interest. The research is conducted by studying the thermodynamics of equilibrium phase relationships in selected transition metal solid solutions, the kinetics of hydrogen uptake and release and the role of surface condition therein for various transition metals, by measuring the fracture characteristics of transition metals containing hydrogen, and by 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, in understanding the process of hydrogen embrittlement, and should contribute to the basic understanding of interstitial solid solutions in metals.

Publications

Journal Articles and Conference Proceedings:

C. S. Pande, R. L. Lyles, Jr., and M. A. Pick, "High Voltage Electron Microscopy of Hydrogen Dissolution in FeTi," Proc. 37th Annual Meeting of the Electron Microscopy Society of America, San Antonio, TX, August 13-19, 1979.

M. A. Pick, J. W. Davenport, M. Strongin, and G. J. Dienes, "Enhancement of Hydrogen Uptake Rates for Nb and Ta by Thin Surface Overlayers," Phys. Rev. Letts. 43, 386 (1979).

Reports:

- BNL 25637^a L. Kaufman and D. Dew-Hughes, "Illustration of Ternary Diagram Synthesis Ti-Fe-Al and Ti-Fe-Mn," AIME Fall Meeting, Milwaukee, WI, September 17-19, 1979.
- BNL 25423^a C. S. Pande and M. A. Pick, "Electron Microscopy of Hydrogen Dissolution in FeTi," Annual TMS-AIME Meeting, New Orleans, LA, February 18-22, 1979.
- BNL 25354^a M. A. Pick and D. O. Welch, "Phase Equilibria and Hydrogen in Dilute Alloys of Vanadium in Niobium," 1979 March Meeting of the American Physical Society, Chicago, IL, March 19-23, 1979; Bull. Am. Phys. Soc. 24, 463 (1979).
- BNL 25986^a M. Strongin and M. A. Pick, "The Enhancement of Hydrogen Uptake Rates in Nb and Ta by Thin Pd Overlayers," 1979 March Meeting of the American Physical Society, Chicago, IL, March 19-23, 1979; Bull. Am. Phys. Soc. 24, 463 (1979).
- BNL 26671 D. Dew-Hughes, "The Addition of Mn and Al to the Hydriding Compound FeTi: Range of Homogeneity and Lattice Parameters," accepted for publication in Met. Trans.
- BNL 26940 M. El-Batanouny, M. Strongin, and M. A. Pick, "The Structure of Pd Overlayers on Nb and Ta and the Relationship to Hydrogen Uptake," accepted for publication in Phys. Rev. Letts.
- BNL 26623 K. S. Lee and D. Dew-Hughes, "The Effect of Hydrogen on the Mechanical Properties of Iron Whiskers," accepted for publication in Met. Trans.
- BNL 24678 M. A. Pick and D. O. Welch, "Hydrogen Absorption in the Niobium-Vanadium System," International Conference on Hydrogen in Metals, Munster, Germany, March 6-9, 1979.
- BNL 25234 M. A. Pick and D. O. Welch, "Hydrogen Absorption in the Niobium-Vanadium System," accepted for publication in Z. fur Phys. Chem. NF.
- BNL 26920 M. A. Pick and M. G. Greene, "The Sticking Coefficient of Hydrogen on Niobium," accepted for publication in Surface Science.
- BNL 26520 M. A. Pick, M. Strongin, and M. G. Greene, "Uptake Rates for Hydrogen by Nb and Ta: Effect of Thin Metallic Overlayers," accepted for publication in J. of Less-Common Metals.

^a Abstract

Title: Effects of Microstructure and
Environment Upon Fracture Toughness

FY 79: \$180,000

Principal Investigators:
S. K. Hwang
D. Gan

FY 80: \$150,000

Sponsor: Basic Energy
Sciences (DOE)

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 size specimens. The study is done by characterizing the development of particular microstructures in commercially pure metals, solid-solutions, and precipitation-hardened alloys under a variety of high-temperature loading conditions and subsequently measuring the fracture toughness. The modes of loading include monotonic creep, and high-temperature stress cycling (fatigue); the important variables are temperature, peak stress or strain, and holding time at peak loads. The microstructure is characterized with optical and electron microscopy, positron annihilation spectroscopy, and with the use of such special facilities available at BNL as small-angle neutron scattering at the High Flux Beam Reactor and x-ray topography at the National Synchrotron Light Source. This study will yield information on the basic aspects of microstructural evolution leading to 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.

Publications

Journal Articles and Conference Proceedings:

A. Arbel, "An Approach to Determining the Useful Life of Materials Loaded at High Temperatures," Scripta Met. 13, 1109 (1979).

Reports:

- BNL 26554 A. Arbel and M. Natan, "The Effect of Various Anodic Coatings on the Creep Behavior of a Strong Aluminum Alloy," accepted for publication in Mat. Sci. and Engr.
- BNL 24992^a A. Arbel and C. S. Pande, "The Effect of Creep on Some Resultant Mechanical Properties of a Solid Solution Nickel Base Alloy," 1979 Annual Meeting of the Metallurgical Society of AIME, New Orleans, LA, February 18-22, 1979.
- BNL 26062^a A. Arbel and C. S. Pande, "The Effect of Strain and Temperature on Resultant Toughness of a Solid Solution Nickel Base Alloy Loaded at Elevated Temperatures," 1979 Fall Meeting of the Metallurgical Society of AIME, Milwaukee, WI, September 16-22, 1979.
- BNL 26052^a A. Arbel, S. K. Hwang, and C. S. Pande, "The Effect of High Temperature Monotonic Loading on Toughness of Some Precipitation Hardening Alloys," 1979 Fall Meeting of the Metallurgical Society of AIME, Milwaukee, WI, September 16-20, 1979.

^aAbstract

Title: Intergranular Stress Corrosion (ISC) of Iron and Nickel-Base Alloys *

FY 79: \$60,000

Principal Investigator:
C. Pande

FY 80: \$60,000

Sponsor: Basic Energy
Sciences (DOE)

ISC in Fe and Ni alloys is a universal problem in the use of these alloys in energy conversion. Its occurrence has been widespread in both fossil- and nuclear-fueled power plants and can be anticipated to occur in advanced reactors, and in solar or geothermal power generators as well. 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 that utilize a steam cycle. Intergranular stress corrosion 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. In this sense there is believed to be a direct competition between the electrochemical dissolution along the grain boundary and the repassivation reactions. An understanding of this competition can lead to improved performance of materials by modifications to their composition and environment. The most important environments to investigate are those that either are oxidizing or contain dissolved caustics.

Publications

Journal Articles and Conference Proceedings:

R. J. Sabatini and C. S. Pande, "A Comparison of Procedures for Quantitative X-Ray Analysis in Thin Films," Proceedings of 14th Annual Conference of the Microbeam Analysis Society, San Antonio, Texas, Aug. 12-17, 1979.

*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.

Title: Basic Processes & Microstructural
Properties of Amorphous Semiconductors

FY 79: \$150,000

Principal Investigator:
R. W. Griffith

FY 80: \$210,000

Sponsor: Basic Energy
Sciences (DOE)

Fundamental investigations will be carried out on 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 insight into limiting processes encountered in a-SC photovoltaic conversion, such as poor minority-carrier transport. Other potential application areas for a-SC materials include microelectronics and a variety of photoelectronic semiconductor devices. The amorphous materials synthesis and characterization will 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. Firstly, basic plasma kinetics and surface reactions that involve radical species will be studied by such techniques as optical emission spectroscopy, molecular absorption spectroscopy, and mass spectrometry. Secondly, 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 that will address the second question include: vibrational spectroscopy, optoelectronic measurements such as of photoluminescence and photoconductivity, and electron microscopy. Studies will be initiated of electronic states and of structural properties at semiconductor surfaces (and interfaces) using photoemission spectroscopy and EXAFS techniques, respectively, at the completed National Synchrotron Light Source.

Publications

Reports:

- BNL 25757 R. W. Griffith, F. J. Kampas, and P. E. Vanier, "The Effects of Impurities on Electronic Properties of Plasma-Deposited Amorphous Silicon Alloys," 21st Electronic Materials Conf. on the Metallurgical Society of AIME, Boulder, CO, June 1979.
- BNL 25766 R. W. Griffith, F. J. Kampas, and P. E. Vanier, "Optical Emission Spectroscopy of Plasma Processes in the Deposition of Amorphous Silicon Alloys," 21st Electronic Materials Conf. of the Metallurgical Society of AIME, Boulder, CO, June 1979.
- BNL 26030 R. W. Griffith, F. J. Kampas, P. E. Vanier, and M. D. Hirsch, "Modifications in Optoelectronic Behavior of Plasma-Deposited Amorphous Semiconductor Alloys via Impurity Incorporation," 8th International Conf. on Amorphous and Liquid Semiconductors, Cambridge, MA, Aug. 27-31, 1979, accepted for publication in J. Non-Crystalline Solids.

Title: Advanced Amorphous Materials
for Photovoltaic Conversion

FY 79: \$ 180,000

Principal Investigator:
R. W. Griffith

FY 80: \$ 200,000

Sponsor: Energy
Technology (DOE)

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 ($\sim 10\%$) 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 a-Si:H MIS Schottky barriers, marginal hole transport is responsible for small values of the short-circuit current density, J_{sc} . Therefore, using advanced plasma deposition techniques, we shall investigate new amorphous semiconductor materials, in which recombination centers are passivated, with the objective of improving minority-carrier transport (and the fill-factor) so that conversion efficiencies of devices may be raised. Materials to be investigated will include variants of the a-Si:H alloy that result, e.g., from research on impurity incorporation which modifies optoelectronic behavior. In addition, it is of interest to survey the properties of new alloys such as valence IV, III, and III-V amorphous semiconductors that are passivated by hydrogenation and/or halogenation. For economic viability, all materials selected must have a sizable resource base, as illustrated by the special case of the alloy a-Si:(F,H). The optoelectronic quality of as-deposited films will be determined with regard to both majority-carrier and minority-carrier transport. For the most promising materials that emerge from the initial optoelectronic characterization, developmental devices such as MIS structures will be fabricated and their conversion efficiencies will be determined.

Publications

Reports:

- BNL 25767 R. W. Griffith, F. J. Kampas, and P. E. Vanier, "The Effects of Impurities on Electronic Properties of Plasma-Deposited Amorphous Silicon Alloys," 21st Electronic Materials Conf. of the Metallurgical Society of AIME, Boulder, CO, June 1979.
- BNL 25766 R. W. Griffith, F. J. Kampas, and P. E. Vanier, "Optical Emission Spectroscopy of Plasma Processes in the Deposition of Amorphous Silicon Alloys," 21st Electronic Materials Conf. of the Metallurgical Society of AIME, Boulder, CO, June 1979.
- BNL 26030 R. W. Griffith, F. J. Kampas, P. E. Vanier, and M. D. Hirsch, "Modifications in Optoelectronic Behavior of Plasma-Deposited Amorphous Semiconductor Alloys via Impurity Incorporation," 8th International Conf. on Amorphous and Liquid Semiconductors, Cambridge, MA, Aug. 27-31, 1979, accepted for publication in J. Non-Crystalline Solids.
- R. W. Griffith, "Advanced Amorphous Materials for Photovoltaic Conversion," Amorphous Silicon/Materials Contractors Review Meeting, RCA Laboratories, Princeton, NJ, May 29 - June 1, 1979.
- R. W. Griffith, M. D. Hirsch, F. J. Kampas, and P. E. Vanier, "Advanced Amorphous Materials for Photovoltaic Conversion," Annual Report to DOE/Solar Technology, October 1, 1978 - September 30, 1979.

PLANS FOR 1980

Most of research programs in this Division are relatively long range basic research efforts in which significant changes in direction or level of effort evolve over a period of time that is generally longer than a year. In that sense, the plans for 1980 are predominantly logical continuations of efforts initiated in 1979, or even earlier. Short descriptions of research plans for 1980 are listed for each program below.

Physical Metallurgy of Metal-Hydrogen Systems

Factors influencing phase equilibria and kinetics in metal-hydrogen systems will be studied. Among these are the role of surface structure and composition, solute-hydrogen interactions in metal solid solutions, and the mechanisms of hydride precipitation and dissolution. Theoretical studies of hydrogen embrittlement will continue.

Relationship between Properties and Structure

The structure and properties of various elementary lattice defects (dislocations, vacancies, interstitials, etc.) in Al₅ compounds will be studied, as will the interaction between applied stress, the structural phase transition, and the superconducting transition in Nb₃Sn. Investigation will continue of the superconducting properties of Al₅ compounds in high magnetic fields, and efforts will be made to develop new, efficient methods to fabricate composite superconductors.

Effect of Microstructure and Environment upon Fracture Toughness

The investigation of the microstructural development under various loading regimes at high temperature and its effect on the ease of crack propagation in solid-solution and precipitation-hardening alloys will continue.

Solar Energy Materials

Future plans include expanded investigations into: plasma chemical reaction that underlie plasma deposition; plasma processing; amorphous semiconductor film growth; and film and device characterization.

Radiation Damage

The study of irradiation effects caused by energetic particles in Al5 compounds and other superconducting materials will continue, including the mechanism of damage to Al5 compounds by high-energy electrons and the kinetics of its subsequent removal by annealing, as well as investigation of the effects of fast-neutron damage to superconducting materials and metallic glasses. Utilization of positron annihilation spectra as a probe of the structure of lattice defects will continue and will include the study of the attack of iron-carbon alloys by hydrogen and the behavior of helium in irradiated metals.

Development of New Experimental Techniques

Preparations will be made for the use of the National Synchrotron Light Source when it becomes available, including the design and construction of a beam line dedicated to extended x-ray absorption fine structure (EXAFS) and photoemission experiments. Preparations will also be made for the use of low-angle neutron scattering (LANS) techniques to characterize microstructures upon completion of the cold-neutron source at the High Flux Beam Reactor.

PROCESS SCIENCES DIVISION

Meyer Steinberg

The program of the Process Sciences Division is concerned with research in chemistry and chemical engineering for development of chemical processes and materials applied to the production of energy and chemical products. The processes presently under investigation include the rapid hydrogenation of coal, the regeneration of sorbents used in desulfurization of combustion gases, the use of non-fossil energy sources particularly nuclear energy (fusion and fission) for the conversion of coal to synthetic fuels. Investigation is also being made of possible Environmental Control Technologies for Atmospheric CO₂ in the mitigation of the potential global CO₂ effect related to fossil fuel usage.

A significant program is being conducted on the development of non-metallic materials of construction for use in geothermal energy production systems. The materials development include cements, polymers, polymer concrete composites and elastomers.

A unique co-polymer of ethylene and SO₂ forming an alternating ethylene polysulfone is under investigation for conversion of a pollutant into a useful mass market polymer as well as conserving an energy intensive hydrocarbon material.

The emphasis of the Process Sciences Division is to investigate advanced and innovative chemical systems and materials for use in energy and chemical production and conversion processes.

SIGNIFICANT ACCOMPLISHMENTS

Significant accomplishments in the process sciences division are listed as follows:

Fossil Energy Programs

In the work on conversion of coal to liquid and gaseous fuels, yields of up to 90% of the carbon converted to synthetic natural gas (SNG pipeline gas) have been obtained by the flash hydrolysis of lignite. A reaction model which fits the data obtained for lignite has been developed and kinetic expressions have been derived. This data can be used to design and develop large scale coal gasification and liquefaction plants.

Commercial silicate cement (Portland Cement Type III) has been found to be a highly effective sorbent for removal of sulfur dioxide under conditions for the fluidized bed combustion (FBC) of coal. The sulfated cement can be regenerated for recovery of sulfur and the sorbent can be recycled for reuse. The use of cement sorbent reduces the requirement for limestone and eliminates the need for disposal of large quantities of calcium sulfate waste.

Ethylene Polymer Conservation

The synthesis of ethylene-sulfur dioxide copolymers has been accomplished with Co-60 gamma radiation and electron beam radiation with very high yields. The characterization of the polymer for a new low cost commercial plastic is being evaluated with industry. Additional benefits of developing this polysulfone polymer include energy conservation and converting of major pollutant SO_2 into a useful product.

Environmental Control Technology for Atmospheric CO_2

An investigation is being conducted of methods for removal, and disposal of CO_2 to prevent atmospheric buildup due to the use of fossil fuel which may result in catastrophic climatic effects (greenhouse effect). The study indicated that removal of CO_2 from the atmosphere is energetically not feasible with a fossil fueled power source. More CO_2 would be generated than removed. Removal of CO_2 from fossil fueled power plant stacks is feasible, however, severe efficiency and economic penalties would be incurred.

Geothermal Materials Program

The Process Sciences Division has assumed responsibility for the DOE programs on the development of nonmetallic materials of construction for use in geothermal energy processes. Research and development work on polymers, polymer concrete composites, and elastomers is in progress. Based upon successful laboratory and field tests performed at geothermal sites throughout the country and economic studies performed concurrent with the research, near-term applications in electric generation and space heating applications in the near future appear practical.

A significant accomplishment at BNL is the development of an organosiloxane polymer-concrete for well cementing that can withstand hot brine conditions up to 350°C.

Concrete-Polymer Materials

The use of concrete polymer materials technology developed at BNL for the repair of concrete structures is rapidly growing throughout the world. During the past year the techniques have been applied to numerous highway bridge decks, roadways, and hydrotechnical structures. Benefits accrued from the use of the materials include reduced life-time costs and energy conservation as a result of reduced transportation delays.

Fusion Energy for the Synthesis and Production of Synthetic Fuels

Process design and analysis of the use of high temperature steam from fusion reactors indicates up to 60% thermal efficiency for hydrogen production using high temperature electrolysis. When combined with high temperature steam gasification of coal, savings of up to 68% of the coal necessary to produce synthetic natural gas can be realized.

Title: Hydrogasification of Coal

FY 79: \$300,000

Principal Investigator:
P. Fallon

FY 80: \$300,000

Sponsor: Fossil Energy (DOE)

The objective of this task is to develop process chemistry data and to investigate methods for improving yields and process conditions for a rapid hydrogasification process. The rapid hydrogasification or hydrothermal liquefaction of coal is a fast gas phase, non-catalytic direct coal conversion technique for the formation of gaseous hydrocarbons and the production of significant quantities of aromatic liquids hydrocarbons. The process variables to be investigated are reactor temperature and pressure, coal type and feed rate, solids and gas residence times and feed gas rates and composition. The technical approach is to contact finely divided coal particles with preheated hydrogen-containing feed gas at high pressure and temperature. The polycyclic structure of the coal molecule is fractured and the hydrogen combines with the free radicals formed, thus increasing the H/C ratio in the product. The products are then rapidly quenched to prevent decomposition and recombination. The equipment used is a 2.5 Kg/hr entrained down-flow tubular reactor system capable of 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 and across the liquid product condensers allow product samples to be taken for study of the effect of residence time on the product yield. Product analysis is obtained with a programmable on-line gas chromatograph calibrated to measure CO, CO₂, CH₄, C₂H₆ and BTX (benzene, toluene and xylene) concentration. Liquid products heavier than C₉ are collected in the condenser traps, measured and characterized at the termination of each experiment. Data reduction and correlation is computerized and the information applied to a kinetic model for the overall reaction. Preliminary process design and analysis is also performed.

Publications

Journal Articles and Conference Proceedings:

M. Steinberg, and P. Fallon, "Coal Processing Technology: Flash Hydropyrolysis of Coal," Chem. Eng. Progress, 75, No. 6, 63-6 (June 1979).

V. Dang and M. Steinberg, "Coal Conversion in Flash Hydropyrolysis Reactors," presented at the 87th National Meeting of AIChE, Boston, Mass., August 19-22, 1979. (BNL 26209R).

M. Steinberg and P. Fallon, "The Flash Hydropyrolysis (FHP) of Coal," presented at the 13th Middle Atlantic Regional Meeting of The Am. Chem. Soc., Monmouth College, West Long Branch, N.J., March 20-23, 1979.

Reports:

BNL 51010 M. Steinberg and P. Fallon, "Flash Hydropyrolysis of Coal," Quarterly Report No. 7, July 1-December 31, 1978. (February 1979).

BNL 51052 M. Steinberg and P. Fallon, "Flash Hydropyrolysis of Coal," Quarterly Report No. 8, January 1-March 31, 1979.

BNL 51107 M. Steinberg and P. Fallon, "Flash Hydropyrolysis of Coal," Quarterly Report No. 9, April 1-June 30, 1979.

M. Steinberg and P. Fallon, "Flash Hydropyrolysis of Coal," Quarterly Report No. 10, July 1-September 30, 1979. (in press).

BNL 26210 P. Fallon, B. Bhatt, and M. Steinberg, "Flash Hydropyrolysis of Lignite and Sub-Bituminous Coals to Both Liquid and Gaseous Hydrocarbon Products," presented at the 178th National Meeting of ACS, Washington, D.C., May 1979, accepted for publication in Fuel.

Title: Alternative Coal Process Schemes

FY 79: \$100,000

Principal Investigator:
M.J. Sansone

FY 80: \$100,000

Sponsor: Fossil Energy (DOE)

The present coal conversion processes are subject to thermal and coal utilization inefficiencies and extremely high capital costs both of which result in high production costs for the gaseous and liquid products. The purpose of this task is to suggest improvements to existing and developing conversion processes and to identify and initiate studies on potentially attractive new conversion concepts. The conversion of coal to synthesis gas is an area of great importance for the production of transportation fuels via indirect liquefaction. It also represents the major portion of the capital costs. The initial effort of the task is directed at a review of existing technology with the purpose of identifying those areas where significant improvements might be realized.

While the major thrust of the program will be in the area of synthesis gas production, it is also proposed to investigate new conversion approaches and to initiate exploratory experimental research into areas which show technical promise but for which data demonstrating feasibility may be lacking.

A study of alternate techniques for the separation of mixtures of methane, hydrogen, and/or carbon monoxide was completed and the results were documented in several reports. These considerations apply to catalytic gasification and hydrogasification schemes in which product methane must be separated from a recycle CO/H₂ stream.

Publications

Reports:

- BNL 51011 M.J. Sansone, A.S. Albanese, and M. Steinberg, "Alternative Process Schemes for Coal Conversion," Progress Report No. 1, February 1979.
- BNL 51075 M.J. Sansone, A.S. Albanese, and M. Steinberg, "Alternative Process Schemes for Coal Conversion," Progress Report No. 2, May 1979.
- BNL 51117 M. Sansone, V. Dang, and M. Steinberg, "Alternative Process Schemes for Coal Conversion," Progress Report No. 3, August 1979.

Title: Regenerative Process for Desulfurization of High Temperature Combustion and Fuel Gases

FY 79: \$250,000

Principal Investigators:
A.S. Albanese
D. Sethi

FY 80: \$290,000

Sponsor: Fossil Energy (DOE)

The objective of this task is to develop regenerable SO₂ sorbents and processes for use in desulfurizing, combustion and fuel gases produced in power generating systems. Applications to fluidized-bed combustion of coal are the more specific goals. To identify the existing problems in FBC and to provide solutions and improvements are essential parts of the task. Fundamental understanding of the kinetics and mechanisms of the reactions in FBC provides the building blocks upon which the process applications can be firmly established. The technical/scientific approach employed to study the regenerative sorbents for FBC are: (1) identify new regenerable SO₂ sorbents for FBC, and obtain information on the rate and capacity of sulfation and regeneration for both fresh sorbent and sorbent which has been cycled, (2) prepare sorbent pellets of a size which could be used in fluidized-bed combustors, and which have acceptable reactivity and high resistance to attrition, (3) operate bench-scale sorbent regeneration equipment (kiln and fluidized beds), (4) understand the physical and chemical factors which account for differences in reactivity among various sorbents, and (5) process design and economic evaluations directed toward the goal of commercial development of new sorbents based on the laboratory experimental work performed. A promising class of sorbents under investigation is calcium silicate cements.

Publications

Journal Articles and Conference Proceedings:

R.T. Yang and M. Shen, "A Regenerative Process for Fluidized-Bed Combustion of Coal with Lime Additives," Ind. Eng. Chem. Process Des. Dev., 18, No. 2, 312-316 (April 1979).

J.M. Chen and R.T. Yang, "Fluidized-Bed Combustion of Coal With Lime Additives. Kinetics and Mechanism of Regeneration of the Lime Sorbent," Ind. Eng. Chem. Fundamentals 18, No. 2, 134-138 (1979).

M. Shen and R.T. Yang, "Direct Evidence for the Existence of Gaseous Intermediates in the CaS-CaSO_4 Reaction," AIChE Journal R&D Notes, AIChE J. 25, No. 3, 547-8 (May 1979).

M. Shen and R.T. Yang, "Calcium Silicates - A New Class of Highly Regenerative Sorbents for Hot Gas Desulfurization," AIChE J. 25, No. 5, 811 (1979).

R.T. Yang and J.M. Chen, "Kinetics of Desulfurization of Hot Fuel Gas with Calcium Oxide. Reaction Between COS and CaO," Env. Sci. Tech. 13, No. 5, 549-53 (May 1979).

Reports:

BNL 50944 M. Shen, J.M. Chen, A.S. Albanese, G. Farber, F.B. Kainz, and J. Pruzansky, "Regenerative Process for Desulfurization of High Temperature Combustion and Fuel Gases," Quarterly Progress Report No. 10, July 1-September 30, 1978. (February 1979).

BNL 50992 M. Shen, A.S. Albanese, G. Farber, F.B. Kainz, and J. Pruzansky, "Regenerative Process for Desulfurization of High Temperature Combustion and Fuel Gases, Quarterly Progress Report No. 11, October 1-December 31, 1979.

BNL 51040 M. Shen, A.S. Albanese, G. Farber, F.B. Kainz, and J. Pruzansky, "Regenerative Process for Desulfurization of High Temperature Combustion and Fuel Gases," Quarterly Progress Report No. 12, January 1-March 31, 1979.

BNL 51106 M. Shen, A.S. Albanese, G. Farber, F.B. Kainz, and J. Pruzansky, "Regenerative Process for Desulfurization of High Temperature Combustion and Fuel Gases," Quarterly Report No. 13, April 1-September 30, 1979.

M. Shen and M. Steinberg, "Mechanistic Study of the Reduction of Calcium Sulfate by Carbon," accepted for publication in J. of Chem. Soc., Chemical Commun., (1979).

M. Shen, J.M. Chen, and M. Steinberg, "The Optimal Temperature of Sulfur Retention," accepted for publication in Thermochimica Acta (1979).

Title: Atmospheric CO₂ Control

FY 79: \$15,000

Principal Investigator:
A.S. Albanese

FY 80: \$40,000

Sponsor: Environmental
Control Technology (DOE)

The objective of this task is to investigate and evaluate methods of controlling the concentration of CO₂ in the atmosphere resulting from fossil energy and other sources.

The approach is (1) to survey alternative environmental control technologies for application to atmospheric CO₂ control, (2) to develop conceptual process schemes for removal, recovery, and disposal of CO₂ from various sources, and (3) to assess and evaluate the control systems in terms of energy efficiency and economic costs.

The process schemes to be investigated include conventional systems and advanced systems.

The sources of CO₂ to be investigated include concentrated and diffuse sources.

The basic data and results are to be documented and made available for formulation of any possible future policy strategies.

Reports:

BNL 50983 M. Steinberg and A.S. Albanese, "Environmental Control Technology for the Flash Hydrolysis of Coal," Progress Report No. 3, April 1, 1978 to December 31, 1978. (February 1979).

BNL 51116 A.S. Albanese and M. Steinberg, "Environmental Control Technology for Atmospheric Carbon Dioxide," (September 1979).

BNL 27164 M. Steinberg and A.S. Albanese, "Environmental Control Technology for Atmospheric Carbon Dioxide," Int. Workshop on the Energy/Climate Interactions, Munster, Germany, March 3-7, 1980.

Title: Geothermal Materials Development

FY 79: \$ 917,000

Principal Investigators:

L.E. Kukacka

D. Van Rooyen

FY 80: \$1,200,000

Sponsor: Division of
Geothermal Energy (DOE)

The lack of durable cost effective materials of construction is a serious problem in the development of geothermal resources for electric generation and direct utilization processes. Specific needs include high temperature sealing materials for use in well logging equipment, pumps, drill bits, packers, and blow-out preventors. Durable materials for drill bits, casing, well cements, pump bearings, process components, equipment foundations and cooling towers are also needed. The goal of the program is to provide DOE/DGE with the technical and managerial basis for the development, testing and practical demonstration of metallic and nonmetallic components for these applications. The work involves in-house research as well as full management of an integrated program involving subcontract efforts and industrial participation. If successfully implemented, the program should have a significant benefit on the economic and environmental aspects of geothermal energy.

Publications

Journal Articles and Conference Proceedings:

N. Carciello, A.N. Zeldin, and L.E. Kukacka, "An Alternate Method of Preparing Polymer Concrete from Mixtures of Liquid and Solid Monomers," J. Appl. Polymer Sci., 24, 2191-2193 (1979).

T. Sugama and L.E. Kukacka, "The Effects of Dicalcium Silicate and Tricalcium Silicate on the Thermal Stability of Vinyl-Type Polymer Concrete," Cement and Concrete Research, 9, No. 1, 69-76, 1979.

T. Sugama, L.E. Kukacka, and W. Horn, "Hydrothermal Stability of Vinyl-Type Polymer Concrete Containing Tricalcium Silicate (C₃S)," Cement and Concrete Research, 9, No. 4, 461-471 (1979).

T. Sugama, L.E. Kukacka, and W. Horn, "Interaction Mechanisms Between Polymethylmethacrylate and Tricalcium Silicate (C_3S)," J. Appl. Polymer Sci., 24, 2121-2135 (1979).

T. Sugama, L.E. Kukacka, and W. Horn, "The Effect of Tricalcium Silicate on the Thermal Stability of Condensation-Type Polymer Concretes," Int. J. Cement Composites, 1, No. 2, 55-62 (1979).

A.N. Zeldin, L.E. Kukacka, and N. Carciello, "Polymer Systems in Geothermal Applications," J. Appl. Polymer Sci., 23, 3179-3191 (1979).

A.N. Zeldin, L.E. Kukacka, J.J. Fontana, N.R. Carciello, and W. Reams, "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., 24, 455-464 (1979).

A.N. Zeldin, L.E. Kukacka, and N. Carciello, "Influence of the Ratio of Styrene and Acrylonitrile in Cross-Linked Polymeric Binders for Use in High Temperature Polymer Concrete Composites," J. Appl. Polymer Sci., 24, 1759-1765 (1979).

A.N. Zeldin, J.J. Fontana, L.E. Kukacka, and N.R. Carciello, "High Temperature Polymer Concretes from Organosiloxane Resins," Int. J. Cement Composites, 1, No. 1, 11-17 (1979).

D.M. Roy, E.L. White, C.A. Langton, and M.W. Grutzeck, "Potential New High Temperature Cements for Geothermal Wells," SPE 7876, Proc. 1979 Society of Petroleum Engineers Symposium on Oilfield and Geothermal Chemistry, January 22-24, 1979.

A. Zeldin, L.E. Kukacka, J. Fontana, and N. Carciello, "Organosiloxane Polymer Concrete for Geothermal Environments," Proc. of 108 AIME Annual Meeting, New Orleans, La., February 18-22, 1979.

J.J. Fontana and A. Zeldin, "Concrete Polymer Materials as Alternate Materials of Construction for Geothermal Applications - Field Test Evaluations," Proc. of 108 AIME Annual Meeting, New Orleans, La., February 18-22, 1979.

Reports:

BNL 51013 L.E. Kukacka, et al., "Cementing of Geothermal Wells," Progress Report No. 11, October-December 1978. (June 1979).

BNL 50979 L.E. Kukacka, et al., "Alternate Materials of Construction for Geothermal Applications," Progress Report No. 17, October-December 1978. (April 1979).

- BNL 51048 L.E. Kukacka, et al., "Cementing of Geothermal Wells," Progress Report No. 12, January-March 1979.
- BNL 51036 L.E. Kukacka, et al., "Alternate Materials of Construction for Geothermal Applications," Progress Report No. 18, January-March 1979.
- BNL 51112 S.V. Cabibbo, R.M. Costello, and T. Ammerlaan, "Economic Assessment of Using Nonmetallic Materials in the Direct Utilization of Geothermal Energy," February 1979.
- BNL 51024 G.L. Kalousek, "Development of Cement for Geothermal Wells," Final Report, March 1, 1979.
- BNL 26864 A. Zeldin, L.E. Kukacka, and N. Carciello, "Effect of Monomer Composition on the Properties of High Temperature Polymer Concretes," to be presented at Am. Chem. Soc., Houston, Texas, March 21-26, 1980.
- BNL 51096 L.E. Kukacka, et al., "Alternate Materials of Construction for Geothermal Applications," Progress Report No. 19, April-June 1979.
- BNL 26727 A.N. Zeldin, L.E. Kukacka, J. Fontana, and N. Carciello, "Properties and Structure of Polymer Concrete Composite Materials with Divinyl Benzene as a Crosslinking Agent," accepted for publication in Polymer Eng. & Sci.
- BNL 26673 T. Sugama, L.E. Kukacka, and W. Horn, "Hydraulic Cement-Type Fillers for Hydrothermally Stable Polymer Concretes," accepted for publication in J. Materials Sci.
- T. Sugama, L.E. Kukacka, and W. Horn, "The Effect of $-C_2S$ /Class H Cement Mixed Fillers on the Kinetics and Mechanical Properties of Polymer Concretes," accepted for publication in Cement and Concrete Research, An International Journal.

Title: Improvement of the Wear-Resistance Properties of Aggregates by Materials Impregnation

FY 79: \$130,000

Principal Investigator:
J.J. Fontana

FY 80: \$ 19,400

Sponsor: Materials Division,
Federal Highway Administration

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.

The objective of the program is to select and evaluate materials and impregnation techniques for improving the wear-resistance properties of natural aggregates. 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 program includes 1) the selection and evaluation of inorganic and organic materials and processes for use in the production of impregnated aggregate, 2) characterization of natural and impregnated aggregates by performance of micro-texture, polishability, wear and weathering tests, 3) performance of field tests, and 4) economic evaluations. With the exception of test track evaluations, the experimental phase of the program is essentially complete and the final report is being prepared.

Title: Concrete Polymer Research on Repair of Deteriorated Concrete

FY 79: \$130,000

Principal Investigator:
J.J. Fontana

FY 80: \$100,000

Sponsor: Implementation
Division, Federal Highway
Administration

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 is to establish 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.

Publications

Journal Articles and Conference Proceedings:

J.J. Fontana and R. Webster, "Thin Sand Filled Resin Overlays," Proc. Second International Congress on Polymers in Concrete, University of Texas at Austin, October 25-27, 1978, 89-104. (January 1979).

J.J. Fontana, R. Webster, and L.E. Kukacka, "Rapid Patching of Deteriorated Concrete Using Polymer Concrete," Proc. Second International Congress on Polymers in Concrete, University of Texas at Austin, October 25-27, 1978, 105-120. (January 1979).

Reports:

BNL 26353 J.J. Fontana and L.E. Kukacka, "Greenport Bridge Reconstruction Using Concrete Polymer Materials," June 1979.

Title: Conservation in the Ethylene Polymer Industry - Polysulfone Copolymers

FY 79: \$100,000

Principal Investigator:
R. Johnson

FY 80: \$135,000

Sponsor: Industrial Energy
Conservation (DOE)

The objectives of this task are to develop useful energy-conserving copolymers of ethylene and sulfur dioxide of the polysulfone type and a process for their production for the plastics industry.

It was shown previously at Brookhaven National Laboratory (BNL) that SO_2 can be copolymerized with ethylene to form polysulfone polymers by a high energy radiation technique. These polysulfone copolymers offer a major potential in conserving valuable petrochemical feedstock by reducing ethylene requirements for the plastics industry while at the same time converting SO_2 , a waste material from the power and metallurgical industry, into a useful product. The use of high energy radiation, either machine or Co^{60} , may be preferred because of the unique process chemistry and resulting product characteristics. Machine radiation may be preferable because of the safety, availability, and investment. The project focuses on the following two major items: (1) establishment of the uniqueness of the radiation process for polysulfone synthesis and (2) determination of the processability and marketability of the substitute polysulfone copolymers. This task is being performed in joint cooperation with an industrial firm, the International Nickel Company (INCO), because of the availability to INCO of large waste quantities of SO_2 from its metallurgical operations and its potential position in the copolymer market. BNL provides the scientific and technical means and experimental facilities for preparation of the copolymer, while INCO provides the analysis and characterization and market expertise for development of an acceptable polymer product.

Publications

Reports:

- BNL 50955 M. Steinberg, R. Johnson, W. Cordes, and D. Goodman,
"Polyketones and Polysulfones for Conservation in the Ethylene
Polymer Industry," Progress Report No. 2, April-September 1978
(December 1979).
- BNL 51034 M. Steinberg, R. Johnson, W. Cordes, and D. Goodman,
"Polyketones and Polysulfones for Conservation in the Ethylene
Polymer Industry," Progress Report No. 4, January-March 1979
(March 1979).
- BNL 51080 M. Steinberg, R. Johnson, W. Cordes, and D. Goodman,
"Polyketones and Polysulfones for Conservation in the Ethylene
Polymer Industry," Progress Report No. 5, April-June 1979
(August 1979).
- M. Steinberg, R. Johnson, W. Cordes, and D. Goodman,
"Polyketones and Polysulfones for Conservation in the Ethylene
Polymer Industry," accepted for publication in Radiation Physics
and Chemistry.

Title: Use of Fusion Energy for the Synthesis and Production of Synthetic Fuels

FY 79: \$300,000 NE (\$30,000 for DEE)

Principal Investigator:
M. Steinberg
J.R. Powell

FY 80: \$500,000 NE (\$30,000 for DEE)

Sponsor: Fusion Energy (DOE)

This work is being conducted in conjunction with the Nuclear energy Department. Fusion reactors are being developed to produce very high temperature steam ranging up to 1400°C. The steam can be used in high temperature electrolytic (HTE) cells to produce hydrogen. Increasing temperatures decreases free energy requirements for the electrolytic decomposition of water. Thermal efficiency for conversion of fusion energy to hydrogen fuel can range up to 60%. When combined with coal high temperature steam gasification and hydrogenation of coal to produce synthetic liquid and gaseous hydrocarbon fuels reduce coal requirements by as much as 68%.

Process design and analysis of the HTE system has been made.

Publications

Journal Articles and Conference Proceedings:

Journal articles are listed in the Nuclear Energy Department.

Reports:

BNL 26710 M. Steinberg, "Synthetic Fuels from Fusion Reactors and Coal," (July 1979).

(Other publications and reports are listed in the Nuclear Energy Department).

PLANS FOR 1980

It is planned to expand the research work on investigation of coal conversion schemes, especially with relation to gasification. Application of non-fossil energy sources for coal conversion will be investigated. A new program on the hydrolysis of biomass (wood and other agricultural products) for conversion to liquid and gaseous fuels will be initiated.

We will continue to take a leading laboratory role in developing non-metallic materials of construction for geothermal energy process applications. Continued research on understanding the interaction between concrete and aggregate in polymer-concrete materials will be conducted.

Evaluation of alternate and advanced techniques for removal, recovery and disposal of CO₂ for environmental control of the potential global CO₂ effect will be performed.