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COVERING THE PERIOD
JANUARY 1978 - DECEMBER 1978

DEPARTMENT OF ENERGY AND ENVIRONMENT

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ABSTRACTS

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PREFACE

This report presents abstracts of all publications in the Energy Sciences programs of the Department of Energy and Environment from January 1, 1978 through December 31, 1978. The mode of publications is indicated on each entry - journal citation, BNL report, or oral presentation.

It is a companion report to "Annual Highlights of Programs in Energy Sciences - (December 1978, BNL 50973)" Together, they present scientific and/or technical highlights of the Energy Sciences programs for the past calendar year, detailed descriptions of all the programs, and the publication issuing from the work performed.

An expression of appreciation is due to all whose efforts were involved in producing this report. First, the individual investigations whose work led to listed publications are to be commended. Secondly, Meyer Steinberg and Masaki Suenaga are to be thanked for their overseeing the production of the text in their respective Division. Finally, and most importantly, the sterling services of a number of secretaries are here acknowledged. Even at the risk of committing an error of omission, particular thanks and appreciation are extended to Sharon Creveling, Ruth Duffy, Toni Fridae, Karen Kalish, Lois Arns, and Pat Taylor.

CHEMICAL SCIENCES DIVISION

PHOTOSYNTHESIS AT 1000 NM: PRIMARY DONORS AND ACCEPTORS

BNL - 23984

J. Fajer, M. S. Davis, J. P. Thornber, and A. Forman

Chemical Sciences Division

The mechanism by which photosynthetic organisms convert light into chemical energy is of considerable interest not only because of the photophysics, chemistry and biology involved but also because of the attractiveness of developing artificial phototransducers modelled on living systems. A combination of optical and paramagnetic spectroscopy, applied *in vivo* and *in vitro* systems, has recently led to a generalized mechanism whereby photosynthetic purple bacteria transduce an impinging photon into the oxidized and reduced species that drive the chemical cycles of the organism:

$$\mathrm{PIX} \xrightarrow{h\nu} \mathrm{P^{*}IX} \xrightarrow{<10\ \mathrm{psec}} \mathrm{P^{+}I^{-}X} \xrightarrow{\sim 200\ \mathrm{psec}} \mathrm{P^{+}IX^{-}}$$

P is a "special pair" of bacteriochlorophylls (BChl), P* is an excited singlet, P^+ a cation radical and X an iron-quinone complex. The nature of I^- is in question; it has variously been considered as the anion of BChl, of bacteriopheophytin (BPh), the free base of BChl, or a complex of both.

This sequence was originally based on data obtained with *Rhodopseudomonas sphaeroides and Chromatium vinosum*, bacteria which contain BChl a. However, a number of photosynthetic bacteria (*Rhodopseudomonas viridis, Thiocapsa pfennigii*, *Ectothiorhodospira halochloris*) utilize a chlorophyll variant, BChl b as the photoactive chromophore to enable them to function at wavelengths as long as 1000 nm.

Experimental and theoretical studies of the anion and cation radicals of BChl b and BPh b are described here compared with data on the oxidized primary donor and reduced acceptor of *Rhodopseudomonas viridis*. The combination of these results with evidence from other laboratories, leads to the conclusion that a common molecular array performs the primary processes in bacteria that contain BChl a or b. On a picosecond time scale, dimers of BChl a (P870) or BChl b (P960), exciton coupled to a second pair of BChls, act as the primary donors. P960 is, however, a dimer with a twist. The most likely candidate as the primary acceptor of the electron photoejected from the BChls is BPh.

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

Program: Porphyrin Chemistry

Sponsor: DOE - Office of Basic Energy Sciences,
Chemical Sciences Division

ANION RADICALS OF PHEOPHYTIN AND CHLOROPHYLL A: THEIR ROLE IN THE PRIMARY CHARGE SEPARATIONS OF PLANT PHOTOSYNTHESIS

BNL - 24618

I. Fujita, M. S. Davis and J. Fajer

Chemical Sciences Division

Optical, electron spin resonance (ESR) and electron-nuclear double resonance (ENDOR) spectra are presented for the anion radicals of chlorophyll a and its metal free base, pheophytin, species which have long eluded characterization because of their reactivity with trace impurities. Features of the ESR and ENDOR spectra are interpreted by molecular orbital computations. Comparison of the emf, optical and magnetic parameters of the anions with those attributed to short-lived transients involved in the primary photoprocesses of plant photosynthesis leads to the conclusion that chlorophyll and pheophytin are the first reduced products of the light-induced charge separations in photosystems I and II, respectively. That mechanism represents a significantly more efficient conversion of incident light into chemical energy than previously assumed and yields strong reductants to drive the biochemistry of both photosystems.

The optical and magnetic results presented provide the guidelines for picosecond laser photolysis, ESR and ENDOR experiments to further test the mechanism proposed.

Fujita, I., Davis, M. S., and Fajer, J. Anion Radicals of Pheophytin and Chlorophyll a: Their Role in the Primary Charge Separations of Plant Photosynthesis. J. Amer. Chem. Soc. 100, 6280-6282 (1978).

Program: Porphyrin Chemistry

Sponsor: DOE - Office of Basic Energy Sciences,
Chemical Sciences Division

PHOTOVOLTAIC PROPERTIES OF METALLOPORPHYRINS

BNL - 24975

Kazuo Yamashita, Frank J. Kampas and Jack Fajer

Chemical Sciences Division

The photoelectrochemical properties of films of metallotetraphenyl-, tetra(n-propyl)-, and octaethyl porphyrins, porphins, co-facial diporphyrins(2) and mesoporphyrin esters have been studied in Al/Porphyrin/Ag and Al/Porphyrin/Fe(CN)$_6^{3-}$,Fe(CN)$_6^{4-}$/Pt cells. For a given porphyrin ligand, quantum efficiencies of the photocurrents parallel the first oxidation potentials of the porphyrins: the more easily oxidized compounds exhibit higher quantum yields. The latter depend on the crystallinity of the porphyrin: films prepared by sublimation were found to be microcrystalline by electron microscopy and yield lower photocurrents than films prepared by solution evaporation which are amorphous.

The current-voltage (I-V) characteristics of the cells resemble those of a metal-insulator-semiconductor diode and are attributed to the photoactive Al-Al$_2$O$_3$-porphyrin interface. At low forward bias voltages, the dark current varies approximately as I-V and at high voltages, the I-V relation becomes superquadratic. The exponent for the dependence of the photocurrent on light intensity ranges between 0.8 and 1.0. These results can be explained by an exponential distribution of traps in the porphyrin film.

Peak quantum yields for the cells investigated range from 10^{-4} to 10^{-1} with power conversion efficiencies varying from 10^{-6} to 10^{-2}.

Yamashita, Kazuo, Kampas, Frank J., and Fajer, Jack. Photovoltaic Properties of Metalloporphyrins. Presented at 177th National Meeting of American Chemical Society, Honolulu, Hawaii, April 1-6, 1979.

Program: Porphyrin Chemistry

Sponsor: DOE - Office of Basic Energy Sciences,
Chemical Sciences Division

LIGATED CHLOROPHYLLS AS PRIMARY DONORS IN PHOTOSYNTHETIC OXYGEN EVOLUTION

BNL - 25181

M. S. Davis, A. Forman, L. K. Hanson, and J. Fajer

Chemical Sciences Division

Magnesium and zinc tetraphenyl chlorins, synthetic models for chlorophyll, exhibit significant variations in the unpaired spin densities of their cation radicals with concomitant changes in oxidation potentials, as a function of solvent and axial ligand. Similar effects are observed for chlorophyll a and its cation radicals. Oxidation potentials for Chl → Chl^+ as high as +0.9V (vs NHE) are observed in nonaqueous solvents with linewidths of the ESR signals of monomeric Chl^+ ranging between 9.2 and 7.8 G in solution. Clearly, the narrowing of ESR linewidths cannot be used as the sole criteria for establishing the existence of dimeric chlorophyll cations in vivo: ENDOR measurements must complement the ESR data. The changes in electronic configuration and ease of oxidation are attributed to mixing of two nearly degenerate ground states of the radicals independently predicted by self-consistent field and extended Huckel molecular orbital calculations.

Comparison of the properties of chlorophyll in vitro with the optical, redox and magnetic characteristics attributed to P680, the primary donor of photosystem II, which mediates oxygen evolution in plant photosynthesis, leads us to suggest that P680 may be a ligated chlorophyll monomer whose function as a phototrap is determined by interactions with its immediate (protein?) environment.

Davis, M. S., Forman, A., Hanson, L. K., and Fajer, J. Ligated Chlorophylls as Primary Donors in Photosynthetic Oxygen Evolution. Biophys. J. (in press).

Program: Porphyrin Chemistry

Sponsor: DOE - Office of Basic Energy Sciences,
Chemical Sciences Division

GRIFFITH MODEL BONDING IN OXYGEN MANGANESE PORPHYRINS

BNL ·· 25193

L. K. Hanson and B. M. Hoffman

Chemical Sciences Division

Manganoglobin, in which manganese porphyrins have been substituted for the heme prosthetic group, cooperatively and reversibly binds some small molecules but not oxygen. However, Mn(II) porphyrins do bind O_2 reversibly at -80^oC in organic solvents to form pentacoordinated complexes in contrast to the hexacoordinated O_2 complexes formed by iron and cobalt porphyrins. The reaction with O_2 transforms the Mn(II) porphyrin spectrum from the normal to "hyper" type with a split Soret band typical of Mn(III) porphyrins. EPR spectra indicate a spin change from $S = 5/2$ to $S = 3/2$, and ^{17}O substitution indicates little unpaired spin density on the O_2. Analysis of the EPR data suggested that the O_2 molecule binds to the Mn in the Griffith mode (edge-on, parallel to the porphyrin plane) and that the complexes could be formally described as $Mn(IV)O_2^=$. However, published ab initio calculations predict instead that $Mn(III)O_2^-$ should be the most stable configuration, with O_2 bound in the Pauling mode (end-on, bent). Charge iterative extended Hückel calculations are reported here for both the Griffith and Pauling models for $O_2 \cdot Mn$ porphins, in which the O-O, Mn-O, out of plane Mn distances and the O-O orientation above the porphinato plane have been varied. All of the experimental results can be explained in terms of the Griffith model but not the Pauling model. Furthermore, our calculations suggest that the ab initio results may simply be due to the use of too short an O-O distance. We conclude therefore that, unlike Co(II) and Fe(II) porphyrins, Mn(II) porphyrins bind oxygen in the Griffith mode in a manner similar to that found for Ti porphyrins.

Hanson, L. K. and Hoffman, B. M. Griffith Model Bonding in Oxygen Manganese Porphyrins. Biophys. J. (in press).

Program: Porphyrin Chemistry

Sponsor: DOE - Office of Basic Energy Sciences,
Chemical Sciences Division

BRIDGED FERROCENES III. THE CRYSTAL AND MOLECULAR STRUCTURE OF 1,1',2,2',3,4,4',5'-TETRAKIS(TRIMETHYLENE)FERROCENE

BNL - 23855

Manny Hillman and Etsuko Fujita

Chemical Sciences Division

The structure of 1,1',2,2',3,4,4',5'-tetrakis(trimethylene)-ferrocene has been determined by x-ray diffraction. This compound forms prismatic crystals of monoclinic space group $P2_1/c$ and four molecules in the unit cell with a = 8.649(4) Å, b = 21.623(2) Å, c = 9.120(1) Å and β = 107.21(3)°. The structure was solved from three dimensional Patterson and Fourier synthesis, and was refined by least squares. The two cyclopentadienyl rings are eclipsed and the dihedral angle between the rings is 11.1°. The iron-carbon distances ranged from 1.997(2) to 2.047(2) Å.

Hillman, M. and Fujita, E. Bridged Ferrocenes III. The Crystal and Molecular Structure of 1,1',2,2',3,4,4',5'-Tetrakis(Trimethylene)Ferrocene. J. Organometallic Chem. 155, 99 (1978).

Program: Investigation of the Chemistry of Energetic Compounds

Sponsor: DOE - Office of Basic Energy Sciences,
Chemical Sciences Division

BRIDGED FERROCENES. I.

BNL - 23856

Manny Hillman, Barry Gordon, Allen J. Weiss and A. P. Guzikowski

Chemical Sciences Division

Previously reported correlations between Moessbauer spectra and the number of bridges in trimethylene bridged ferrocene derivatives have now been observed in the reduction potentials and in the electronic spectra. Crystallographic results reported in the subsequent papers of this series are employed to confirm the previous attribution of these effects to ring-ring tilting, iron-to-ring distance, and to a lesser extent the non-planarity of the rings in some compounds. Rearrangement during the bridging reaction is proposed to explain the failure of the formation of the four-bridged compound.

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

Program: Investigation of the Chemistry of Energetic Compounds

Sponsor: DOE - Office of Basic Energy Sciences,
Chemical Sciences Division

BRIDGED FERROCENES II. THE CRYSTAL AND MOLECULAR STRUCTURE OF 1,1',2,2', 4,4'-TRIS (TRIMETHYLENE) FERROCENE

BNL - 23857

Manny Hillman and Etsuko Fujita

Chemical Sciences Division

The crystal and molecular structure of 1,1',2,2',4,4'-tris-(trimethylene) ferrocene has been determined by x-ray diffraction. This compound forms monoclinic needles of space group C2/c with sixteen molecules in the unit cell, a = 30.899(6) Å, b - 9.416(1) Å, c = 25.145(1) Å and β = 127.31(1)°. The structure was solved from three-dimensional Patterson and Fourier syntheses and was refined by least squares. The structure consists of two crystallographically independent molecules showing similar geometries. The two cyclopentadienyl rings are eclipsed and the dihedral angle between the two rings is 2.4°. The average iron to ring-carbon distance is 1.992 Å. The distance between the rings (3.15 Å) is significantly shorter than in ferrocene, and the rings appear to be slightly non-planar.

Hillman, M. and Fujita, E. Bridged Ferrocenes II. The Crystal and Molecular Structure of 1,1',2,2',4,4'-Tris(Trimethylene)Ferrocene. J. Organometallic Chem. 155, 87 (1978).

Program: Investigation of the Chemistry of Energetic Compounds

Sponsor: DOE - Office of Basic Energy Sciences,
Chemical Sciences Division

BRIDGED FERROCENES IV. THE CRYSTAL AND MOLECULAR STRUCTURE OF 1,1',2,2',3,3',4,5,4',5'-PENTAKIS(TRIMETHYLENE)FERROCENE

BNL - 23861

L. D. Spaulding, G.J.B. Williams, and M. Hillman

Chemical Sciences Division

The title compound (molecular formula $C_{25}H_{30}Fe$) forms prismatic crystals from hexane which belong to the monoclinic space group $P2_1/n$ with lattice constants $a = 9.486(2)$ Å, $b = 12.134(2)$ Å, $c = 16.024(2)$ Å, $\beta = 93.12(1)^{\circ}$, and $Z = 4$. The structure was solved by the heavy atom method and refined by full-matrix least squares against 3839 F^2 terms to yield $R = 0.08$ and $R_w = 0.12$. The Fe to cyclopentadienyl ring-carbon distances range from 1.985(3) Å to 2.042(4) Å. The two cyclopentadienyl rings are eclipsed, they are slightly non-planar, and the angle between their least-squares planes is 12.5°.

Spaulding, L. D., Williams, G.J.B., and Hillman, M. Bridged Ferrocenes IV. The Crystal and Molecular Structure of 1,1',2,2',3,3',4,5,4',5'-Pentakis-(Trimethylene)Ferrocene. J. Organometallic Chem. 155, 109 (1978).

Program: Investigation of the Chemistry of Energetic Compounds

Sponsor: DOE - Office of Basic Sciences,
Chemical Sciences Division

AEROSOL FORMATION ON THE FLASH PHOTOLYSIS OF SO_2/GAS MIXTURES

BNL - 24442

L. D. Fogel and J. W. Sutherland

Chemical Sciences Division

A long-lived transient absorption (decay $t_{1/2}$ ~300 sec at 1 atm) observed on the flash photolysis (energies electrical ≤ 200 joules) of SO_2/gas mixtures has been identified as resulting from light scattering from H_2SO_4 aerosols. No detectable signals were monitored on photolysis at $\lambda > 240$ nm, indicating that the aerosol precursors must result from photodissociation, $SO_2\ (X^1A_1) + h\nu(\lambda < 218 \text{ nm}) \rightarrow SO(^3\Sigma^-) + O(^3P)$. At high pressures, the $O(^3P)$ reacted either with SO_2 to form SO_3 or with O_2 to yield O_3, which was stable for times ≤ 40 min. Under these conditions, the O_3 yield served as an internal monitor of flash intensity. In O_2, the SO was oxidized to SO_3. With even traces of H_2O vapor, SO_3 was hydrated immediately to form H_2SO_4 vapor, which quickly underwent heteromolecular homogeneous nucleation. Nucleation was quenched rapidly as the acid vapor was consumed by further nucleation, by condensation and by vapor diffusion to the cell walls. A model was formulated in which condensation was considered kinetically negligible and the particles grew by coagulation; simultaneously, they were lost by tranquil gravitational settling and by diffusion to the walls. Computer simulations demonstrated that the observed time dependence of the absorbance data could be accounted for by this scheme. The model also described the pressure, temperature and wavelength dependencies of the results. The application of the flash photolysis technique to produce relatively high concentrations of supersaturated vapors in times very short compared to those for aerosol formation will be discussed.

Fogel, L. D. and Sutherland, J. W. Aerosol Formation on the Flash Photolysis of SO_2/Gas Mixtures. Presented at the 175th Meeting of the American Chemical Society, Miami Beach, Florida, September 1978.

Program: Kinetics and Mechanism of Chemical Processes Related to the Development and Use of Energy

Sponsor: DOE - Office of Basic Energy Sciences,
Chemical Sciences Division

AEROSOL FORMATION ON THE FLASH PHOTOLYSIS OF SO_2/GAS MIXTURES

BNL - 25021

L. D. Fogel and J. W. Sutherland

Chemical Sciences Division

A long-lived transient absorption observed on the flash photolysis of SO_2/gas mixtures at $\lambda \geq 190$ nm has been identified as resulting from light scattering by H_2SO_4 aerosols. No detectable signals were monitored on photolysis at $\lambda \geq 270$ nm, indicating that the aerosol precursors originated from the promotion of SO_2 into its second singlet level and into its dissociation continuum. The SO_3 that was formed was hydrated immediately to yield H_2SO_4 vapor in a highly supersaturated state and heteromolecular homogeneous nucleation to produce H_2SO_4 aerosols ensued. This nucleation was quenched rapidly as the acid vapor was consumed by further nucleation, by condensation and by vapor diffusion to the cell walls. A model was formulated in which the condensations of the H_2SO_4 and the H_2O vapors on the growing droplets were considered kinetically negligible and the particles grew by coagulation; simultaneously, they were lost by tranquil gravitational settling and by diffusion to the cell walls. Computer simulations demonstrated that the observed time dependence of the absorbance data (measured at a fixed wavelength) could be accounted for by this scheme. The effects of temperature, pressure and wavelength (of the analyzing light) were also described satisfactorily by this model.

Fogel, L. D. and Sutherland, J. W. Aerosol Formation on the Flash Photolysis of SO_2/Gas Mixtures. J. Chem. Phys. (in press).

Program: Kinetics and Mechanism of Chemical Processes Related to the Development and Use of Energy

Sponsor: DOE - Office of Basic Energy Sciences,
Chemical Sciences Division

RATE CONSTANT FOR THE REACTION OF $O(^3P)$ ATOMS WITH ETHYLENE

BNL - 25180

Edward G. Skolnik and R. Bruce Klemm

Chemical Sciences Division

The important standard kinetic reaction,

$$O(^3P) + C_2H_4 \rightarrow CH_3 + HCO,$$

has been studied by the discharge flow-resonance technique over the temperature range 298-750°K. Experiments were performed under pseudo-first order conditions, $\left[([C_2H_4]/[O]) \geq 50;\ [O]_o = 5\text{-}20 \times 10^{10}\ \text{atoms/cm}^3\right]$, following the decay of $O(^3P)$ atoms as a function of distance (α time) in the flow tube. Particular care was taken to exclude the effects of possible secondary reactions so as to remove the need for a stoichiometric correction. The rate data for this reaction was found to fit the Arrhenius expression:

$$k = (8.7 \pm 1.0) \times 10^{-12} \exp - \left[(1300 \pm 110)/RT\right]\ \text{cm}^3\text{molec}^{-1}\text{s}^{-1}$$

These results will be compared to those from previous studies, and a review of a sizable body of kinetic data on this reaction will be made.

Skolnik, E. G. and Klemm, R. B. Rate Constant for the Reaction of $O(^3P)$ Atoms with Ethylene. Presented at 177th National Meeting of American Chemical Society, Honolulu, Hawaii, April 1-6, 1979.

Program: Combustion Studies on Alternative Fuels

Sponsor: DOE - Office of Basic Energy Sciences,
Chemical Sciences Division

ABSOLUTE RATE PARAMETERS FOR THE REACTION OF GROUND STATE OXYGEN ATOMS WITH ACETALDEHYDE

BNL - 25192

R. Bruce Klemm and Edward G. Skolnik

Chemical Sciences Division

The bimolecular rate coefficient for the reaction,

$$O(^3P) + CH_3CHO \xrightarrow{k_1} OH + CH_3CO,$$

was measured directly over a wide range in temperature and total pressure utilizing two independent experimental techniques. With the flash photolysis-resonance fluorescence method, k_1 was determined at total pressures in argon diluent of 50 to 400 torr and at six temperatures over the range: 298 to 507 K. A lower range in total pressure, 1-3 torr, and a wider range in temperature, 298-748 K, were afforded using the discharge flow-resonance fluorescence technique. For the range (298-500 K) where the temperatures overlapped, the two techniques yielded virtually the same Arrhenius expression, with an activation energy of approximately 2040 ± 180 cal/mole and a pre-exponential factor of about $(1.8 \pm 0.6) \times 10^{-11}$ $cm^3 molec^{-1} s^{-1}$. These results will be compared to those of previous studies of this reaction and the bond energy-activation energy correlation for O-atom/aldehyde reactions of Singleton, et al. will be discussed with particular emphasis on the present data as well as some recent kinetic results on the $O(^3P) + H_2CO$ reaction.

Klemm, R. B. and Skolnik, E. G. Absolute Rate Parameters for the Reaction of Ground State Oxygen Atoms with Acetaldehyde. Presented at 177th National Meeting of American Chemical Society, Honolulu, Hawaii, April 1-6, 1979.

Program: Combustion Studies on Alternative Fuels

Sponsor: DOE - Office of Basic Energy Sciences,
Chemical Sciences Division

METAL HYDRIDES AND ENERGY STORAGE

BNL - 23859

J. J. Reilly

Chemical Sciences Division

Many metals and alloys will react directly and reversibly with hydrogen to form metal hydrides. Several such hydrogen-metal alloy systems have pressure-temperature-composition characteristics which are attractive for energy storage applications. A brief outline of metal hydride chemistry will be given. All of the systems of interest involve intermetallic compounds or metal alloys and note will be made of the competing thermodynamic and structural influences which obtain in such cases. The pertinent properties of specific compounds will be discussed and compared with other hydrogen or energy storage options. Finally, engineering-scale demonstrations using iron titanium hydride as a source of hydrogen fuel for both automotive and stationary applications will be described.

Reilly, J. J. Metal Hydrides and Energy Storage. Bull. Amer. Phys. Soc. 23(3), 295 (1978).

Program: Metal Hydrides

Sponsor: DOE - Office of Basic Energy Sciences,
Chemical Sciences Division

THE SOLUTION OF HYDROGEN IN BINARY ALLOYS: INTERMETALLIC COMPOUNDS VS. RANDOM ALLOYS

BNL - 24075

James F. Lynch

Chemical Sciences Division

The solution of hydrogen in the low-temperature modification of $TiCr_2$ (C-15 structure) has been investigated in detail. Some of the results obtained in the region of dilute solution will be presented. The behavior exhibited by intermetallic/hydrogen systems is markedly different from that of hydrogen in pure metals or in random binary alloys. Some of these differences will be discussed in light of the $TiCr_2/H_2$ system.

Lynch, James F. The Solution of Hydrogen in Binary Alloys: Intermetallic Compounds vs. Random Alloys. Presented at Albuquerque Hydride Meeting, Sandia Labs., Albuquerque, New Mexico, March 8 and 9, 1978.

Program: Metal Hydrides

Sponsor: DOE - Office of Basic Energy Sciences,
Chemical Sciences Division

SYNTHESIS, PROPERTIES AND APPLICATIONS OF SOME USEFUL METAL HYDRIDES

BNL - 24080

J. J. Reilly and J. R. Johnson

Chemical Sciences Division

Many metals and metal alloys will react directly and reversibly with hydrogen to form a metal hydride. Several such metal-hydrogen systems have properties which appear attractive as energy storage media. The first part of the talk will be concerned with a brief outline of metal hydride chemistry after which emphasis will be focused on the reaction of intermetallic compounds with hydrogen, the use of thermodynamic and metallurgical criteria to predict reaction paths, the properties of several systems of interest and their practical applications.

Reilly, J. J. and Johnson, J. R. Synthesis, Properties and Applications of Some Useful Metal Hydrides. Presented at Albuquerque Hydride Meeting, Sandia Labs., Albuquerque, New Mexico, March 8 and 9, 1978.

Program: Metal Hydrides

Sponsor: DOE - Office of Basic Energy Sciences
Chemical Sciences Division

THE DILUTE SOLUTION OF HYDROGEN IN TITANIUM/MOLYBDENUM ALLOYS

BNL - 24717

James F. Lynch and John Tanaka

Chemical Sciences Division

The solution of hydrogen in a series of random bcc titanium/molybdenum alloys has been examined over the temperature range 650 K - 1000 K, for samples of Mo content ranging from 45 to 65 atom %. We observe behavior which is atypical of hydrogen dissolved in random binary alloys. Of particular interest are the following points:

i) these systems conform to Sieverts' Law (i.e., $P_{H_2}^{\frac{1}{2}} = K_s(H/M)$ only in the very dilute region, to H/M $\sim 1 \times 10^{-2}$. Thereafter, deviations in the direction of decreased hydrogen solubility are observed.

ii) the relative partial molar enthalpy of hydrogen in the alloy increases (becomes less exothermic) with increasing hydrogen content.

iii) plots of $\Delta\overline{G}_H^{xs}$ against hydrogen content are approximately linear; however, these plots exhibit positive slopes, suggesting H-H repulsions.

Other aspects of the data are in conformity with typical hydrogen/random binary alloy systems. Thus, for example, the standard partial molar enthalpy of hydrogen solution decreases linearly with increasing lattice parameter of the parent alloy. The partial molar entropy of solution decreases with increasing Mo content, suggesting that molybdenum atoms block interstitial sites for hydrogen occupation at low hydrogen contents.

Lynch, James F. and Tanaka, John. The Dilute Solution of Hydrogen in Titanium/Molybdenum Alloys. Presented at Hydrogen in Metals Symposium, Münster, Germany, March 12-17, 1979.

Program: Metal Hydrides

Sponsor: DOE - Office of Basic Energy Sciences,
Chemical Sciences Division

THE ABSORPTION OF HYDROGEN AND DEUTERIUM BY (C-15) $TiCr_2$

BNL - 24718

James F. Lynch, John R. Johnson, and James J. Reilly

Chemical Sciences Division

The dilute solution of hydrogen (deuterium) in the low temperature allotrope of the intermetallic compound $TiCr_2$ has been investigated over a range of temperatures from 272.2 K - 757.0 K. Pronounced positive deviations from Sieverts' Law were observed in the pressure-composition-temperature relationships over the range of pressures and temperatures examined. The relative partial molar enthalpy of hydrogen (deuterium) absorption was found to increase (i.e., become less exothermic) with solute content; the enthalpy was independent of temperature over the range studied here. Examination of $\Delta\overline{G}^{xs}$-solute content relationships suggests H-H repulsive interactions. Examination of thermodynamic data obtained from the p-c-T relationships indicates that for $T \lesssim 590$ K, an inverse solubility isotope effect is observed (i.e., deuterium solution more stable than hydrogen solution). A comparison of hydrogen and deuterium solubilities suggests that the vibrational frequency of H atoms in the $TiCr_2$ lattice is $\gamma \sim 1600$ cm^{-1}.

Lynch, James F., Johnson, John R., and Reilly, James J. The Absorption of Hydrogen and Deuterium by (C-15) $TiCr_2$. Presented at Hydrogen in Metals Symposium, Münster, Germany, March 12-17, 1979.

Program: Metal Hydrides

Sponsor: DOE - Office of Basic Energy Sciences,
Chemical Sciences Division

THE SUPERIONIC FLUORITE STRUCTURE: A NEUTRON DIFFRACTION STUDY OF PbF_2 AND BaF_2

BNL - 24954

F. Reidinger, J. D. Axe, S. M. Shapiro, N. Wakabayashi

Chemical Sciences Division

For many compounds with the fluorite structure a specific heat anomaly accompanied by a large increase of the anion mobility signals the transition from an ordered to a disordered structure. Neutron powder diffraction studies were carried out between 23 and 750°C for PbF_2 and 23 and 1050°C for BaF_2. In addition a neutron data set of a single crystal of PbF_2 was obtained and analysed. Analysis of the high temperature data reveals a decrease of fluorine density at the normal site ($\frac{1}{4}\frac{1}{4}\frac{1}{4}$) and a build up around sites at xxx, x = .33 and .43(1), and at $\frac{1}{4}\frac{1}{4}\frac{1}{2}$. The last site was found to be occupied only at 502 and 598°C. Even though the 3rd order parameter of F is highly significant at 23°C for the single crystal data set, the powder data, because of limited resolution, reveal significant anharmonic effects only at 400°C for F and at 705 and 750°C for both F and Pb. While the interstitial occupanices do not follow a simple temperature dependence, the depopulation of the $\frac{1}{4}\frac{1}{4}\frac{1}{4}$ site is linear with two different slopes: between 350 and 450°C, the temperature range of the specific heat anomaly, the slope is 0.3% per °C; between 450 and 750°C it is 0.06% per °C. By extrapolation we find that at 855°C, the melting point, only about 40% of the $\frac{1}{4}\frac{1}{4}\frac{1}{4}$ sites are occupied. The slope of U_{11} of F versus temperature increases sixfold at about 200°C, a temperature which is well below the lower limit of the specific heat anomaly, where the temperature dependence of U_{11} of Pb increases by the same factor. For BaF_2 only the data set at 1150°C was in the superionic phase. We found significant density at the two xxx sites, x = .33(1) and .47(2).

We conclude: occupancy of interstitial sites is characteristic for the superionic fluorites. Occupancy of sites with different metal-fluorine distances indicates a temperature dependence of the corresponding pair potentials.

Reidinger, F., Axe, J. D., Shapiro, S. M., and Wakabayashi, N. The Superionic Fluorite Structure: A Neutron Diffraction Study of PbF_2 and BaF_2. Presented at 36th Annual Pittsburgh Diffraction Conference, Pittsburgh, Pa., October 26-27, 1978.

Program: Metal Hydrides

Sponsor: DOE - Office of Basic Energy Sciences,
Chemical Sciences Division

SINGLE-CRYSTAL NEUTRON DIFFRACTION STUDIES OF GROUP VA METAL HYDRIDES (DEUTERIDES)

BNL - 24955

F. Reidinger, J. J. Reilly and R. W. Stoenner

Chemical Sciences Division

Analysis of 34 high-resolution data sets (typical R-factors are about 0.6%) at different temperatures and H(D) concentrations yielded the following results:

1) The anisotropic mean-square displacements (MSDs) U11 and U22 (U33=U22) of H(D) at ($\frac{1}{4}0\frac{1}{2}$) in the bcc unit cell depend on temperature and concentration. For V alloys U11/U22 is always larger than 2.0 and increases strongly with temperature. For Nb and Ta alloys U11/U22 decreases with increasing concentration and is expected to reach 1.0 at the upper limits of the α' phase. However for TaH(D)x in the α phase and for sufficiently dilute alloys of NbH(D) U11/U22 and U(H)ii/U(D)ii approach the respective classical values of 2.0 and 1.0 and not 1.41 as predicted by the widely accepted quantum mechanical model. At 90°C the Uii of H(D) in TaH.20(TaD.13) can be calculated from the formula Uii(H,D) = .087(eV)/$m\omega_i^2$ with the appropriate mass m and frequency ω. This is a manifestation of the equi-partition theorem, which is generally thought to be limited to the classical regime. However, H(D) in these metals is not a classical oscillator. We predict that at sufficiently low temperatures U22 of H in TaHx will be significantly less than the MSD of the corresponding quantum oscillator due to the latter's zero-point energy. We conclude that the energies of the vibrational modes of H(D) during its rest phase are not given by the eigen values of the corresponding Schroedinger equation.

2) Anharmonicity of the site potential at ($\frac{1}{4}0\frac{1}{2}$) is evident from density at (.32,0,.44) which is present in all alloys except TaH.20 and TaD.13. Significant (H(D) density, which was refined by a partial atom approach, was found at the octahedral site for NbDx and TaDx, at the trigonal site for all hydrides and at both sites for VDx. If these partial atoms are interpreted as intermediate states of a mobile atom, the diffusion path leads through the octahedral site for NbDx and TaDx, the trigonal site for all hydrides and through both sites for VDx. However, a consistent dependence of the population of these sites on the activation energy of diffusion could not be found. For TaH.20 and TaD.12 there is slight evidence for additional density at (.3,0,0) and (.4,0,0) respectively. We found no indication of the presence of higher excited states of H(D) which might be expected in view of the anomalous U11/U22 ratios.

3) The initial increase of the isotropic MSDs of the host atoms generally levels off at higher H(D) concentrations. However, for TaD.79 at 110°C U11 of Ta is smaller than U11 of the pure metal at the same temperature. There is evidence in TaH.20 and NbH.82 of 4th order anhormonic distortions of both metal and H(D) sublattices which we interpret as premonitory effects of the transition to a partially ordered phase.

Reidinger, F., Reilly, J. J., and Stoenner, R. W. Single-Crystal Neutron Diffraction Studies of Group VA Metal Hydrides (Deuterides). Presented at 36th Annual Pittsburgh Diffraction Conference, Pittsburgh, Pa., October 26-27, 1978.

Program: Metal Hydrides

Sponsor: DOE - Office of Basic Energy Sciences,
Chemical Sciences Division

ON THE δ-α' PHASE TRANSITION OF $TaD_{.77}$

BNL - 24964

F. Reidinger and J. J. Reilly

Chemical Sciences Division

A single domain crystal of $TaD_{.77}$ was studied by neutron diffraction in the δ and α' phase. The space group of orthorhombic $TaD_{.77}$ is Cccm, with Ta on the 4e sites and, at 24°C, 0.749(5) D on the 4a sites, 0.007(9) D on the 4b and 0.015(3) D on the 16m sites. From the lattice constants, a = 3.4517(6), b = 4.775(1) and c = 4.819(1), we conclude that the interaction between deuterons is repulsive. The transition to the α' phase occurs in two stages. The first is an order-disorder transition with increasing amounts of D being distributed equally among the 4b and 16m sites. The order parameter follows a power law with $T_c \gtrsim 96°C$ and an exponent of .11(1). Third and fourth order anharmonic parameters are significant even at 23°C and some increase strongly as the phase boundary (∿96°C) is approached. At 94°C the thermal parameters Uii and the ratios U11/U22 ($U33 \cong U22$) of D on the main site differ significantly from the corresponding values of D at the secondary sites. The appearance of multiple twinning at 97°C interrupts the continuous transition from Cccm to Cmmm. This second stage of the transition is due to the α'-δ two phase region. At 110°C the crystal is completely in the α' phase with the space group Im3m (a = 3.4111(5) Å). During this transition U11 of D on the 4a site increases abruptly from .0160(6) to .0209(4) $Å^2$, whereas U22 (.0110(4) $Å^2$) and the Ta-D distance increase continuously. Anharmonic fourth order effects are absent in the α' phase, but D has a significant third order parameter. Most of D, 98.7(3)%, occupies tetrahedral sites with the remainder occupying octahedral sites. In the δ phase, however, no significant density was found on the latter type of sites.

Reidinger, F. and Reilly, J. J. On the δ-α' Phase Transition of $TaD_{.77}$. Presented at Annual Meeting of Metallurgical Society, New Orleans, La., February 18-22, 1979.

Program: Metal Hydrides

Sponsor: DOE - Office of Basic Energy Sciences,
Chemical Sciences Division

SINGLE CRYSTAL PREPARATION AND CHARACTERIZATION OF THE GROUP V A METAL HYDRIDES AND DEUTERIDES

BNL - 24965

F. Reidinger, J. J. Reilly and R. W. Stoenner

Chemical Sciences Division

Single crystals of the Group V A (vanadium group) hydrides and deuterides have been prepared. The quality of the specimens, as assessed by X-ray and neutron diffraction techniques, was usually sufficient for detailed structural analyses which are currently in progress. It was noted in many cases that the single crystal hydride (deuteride) could be cycled through the α'-δ phase transition without a deterioration in crystal quality. In one case a single domain, single crystal of $TaD_{0.79}$ (δ phase) was successfully produced.

Reidinger, F., Reilly, J. J., and Stoenner, R. W. Single Crystal Preparation and Characterization of the Group VA Metal Hydrides and Deuterides. Scripta Metallurgica (submitted).

Program: Metal Hydrides

Sponsor: DOE - Office of Basic Energy Sciences,
Chemical Sciences Division

A SINGLE-CRYSTAL NEUTRON-DIFFRACTION STUDY OF NbH.82 IN THE SUPERIONIC PHASE

BNL- 25397

F. Reidinger, J. J. Reilly and R. W. Stoenner

Chemical Sciences Division

The high-resolution ($\sin\theta_{max}/\lambda=1.2$) and high-precision study (R_F=.3%) at 119°C confirms the tetrahedral interstices (¼0½) of the bcc lattice as the favored equilibrium sites for H. The mean-square displacement (MSD) of Nb (.0059(1)Å^2) is about 20% smaller than U11 of pure Nb, and a fourth order component D1111 is now present. The anisotropic MSDs of H, U11=.0306(7), U22=.0167(2) (U33=U22), are larger than the respective values of .0182 and .0129 predicted by the simple quantum harmonic oscillator model from the observed energies of the corresponding localized modes. In particular the value of 1.84(5) for U11/U22 questions the applicability of the textbook model. Anharmonic effects, although too small to account for such a discrepancy, are still significant: residual density at .42,0,.34, characteristic of tetrahedral site symmetry, can be fully described by a third order parameter, while density at 3/8,0/3/8 is best described by 2.5(3)% of a H. We interpret D2222, the largest fourth order parameter of H, and the anharmonic distortion of Nb as premonitory effects of the α'-β transition at 117°C. The density at the saddle point, 3/8,0,3/8, cannot be related by a Boltzman factor to the activation energy of diffusion, but is consistent with a hopping mechanism, if a ratio of about 1:50 is assumed for the ratio between hopping and localized frequencies. Diffusion via an extended intermediate state or band states is inconsistent with the present probability density of H which can be uniquely represented by a partial Fourier synthesis.

Reidinger, F., Reilly, J. J., and Stoenner, R. W. A Single-Crystal Neutron-Diffraction Study of NbH.82 in the Superionic Phase. Presented at American Crystallographic Association Meeting, Honolulu, Hawaii, March 26-30, 1979.

Program: Metal Hydrides

Sponsor: DOE - Office of Basic Energy Sciences,
Chemical Sciences Division

MECHANOCHEMICAL EFFECTS IN COAL CONVERSION. 1. COAL HYDROGENATION IN GASEOUS HYDROGEN AIDED BY MECHANICAL ENERGY

BNL - 24370

Ralph T. Yang

Chemical Sciences Division

Hydrogenation experiments with a Pennsylvania anthracite coal were carried out in H_2 under the following conditions: with simultaneous grinding; with grinding and the addition of 1% tin; without simultaneous grinding; and without grinding but with the addition of $SnCl_2$ (1% Sn). Temperature was maintained at 442°C and pressure at 1000 psig (∿6.8 MPa). By eliminating or minimizing the effects of heating due to grinding and of size and mass transfer, the net effects on hydrogenation of the above conditions were examined. $SnCl_2$, as expected, increased the light products, both gaseous and liquid. Grinding substantially increased the heavy oil products (MW ∿280), but not the light fractions. The effect of grinding in combination with the addition of tin was very similar to the effect of $SnCl_2$. A simple mechanistic scheme is postulated to represent these effects. Rationale of the mechanochemical effects is presented. Some preliminary results of the ESR measurements regarding these effects are also included.

Yang, Ralph T. Mechanochemical Effects in Coal Conversion. 1. Coal Hydrogenation in Gaseous Hydrogen Aided by Mechanical Energy. Fuel (submitted).

Program: Chemistry and Physics of Coal Utilization

Sponsor: DOE - Office of Basic Energy Sciences,
Chemical Sciences Division

A MECHANISTIC STUDY OF THE HYDROGENATION/DEHYDROGENATION OF SOME HYDROAROMATICS

BNL - 24575

T. Gangwer, S. Casano, and D. MacKenzie

Chemical Sciences Division

The kinetics of the tetralin/1,2 dihydronaphthalene/naphthalene system in the gas phase were studied. The reactions were found to be heterogeneous and followed zero order rate laws in our quartz vessels. The rate constants measured for initial tetralin conversion to 1,2-dihydronaphthalene plus hydrogen and for initial 1,2-dihydronaphthalene conversion to naphthalene plus hydrogen were 3.1×10^{-9} M min^{-1} cm^{-2} and 4.6×10^{-10} M min^{-1} cm^{-2}, respectively. A mechanistic model is proposed for the system and the nature of the heterogeneous sites are discussed.

Gangwer, T., Casano, S., and MacKenzie, D. A Mechanistic Study of the Hydrogenation/Dehydrogenation of Some Hydroaromatics. J. Phys. Chem. (submitted).

Program: Chemistry and Physics of Coal Utilization

Sponsor: DOE - Office of Basic Energy Sciences,
Chemical Sciences Division

HYDROGEN TRANSFER MECHANISMS RELEVANT TO COAL LIQUEFACTION

BNL - 25227

Tom Gangwer

Chemical Sciences Division

The use of hydroaromatic solvents to convert coal to liquid products is the basis of several coal conversion processes. Although the time dependence of coal liquefaction for these systems has been studied, interpretation of the reported concentration time profiles in terms of specific chemical reaction sequences has not been feasible for such complex mixtures. Yet some specific mechanistic detail is needed to gain insight into coal liquefaction chemistry for the purpose of improving conversion processes. This talk will present results from an ongoing study into the chemistry which is the basis of liquefaction: the mechanism by which hydroaromatic molecules transfer hydrogen.

The system studied was tetralin/dihydronaphthalenes/naphthalene at 400°C. This system undergoes reactions which are typical of the hydrogen transfer chemistry occurring during coal liquefaction. The mechanistic details of this system will be presented. The value of the insite gained from this phase of the program in laying a foundation on which to build an understanding of the complex liquefaction chemistry will be discussed.

In the liquefaction process, the mineral matter present in the reacting coal may be providing catalytic surfaces for hydrogenation-dehydrogenation. A number of the minerals commonly found in coal have been studied for their catalytic effects on the tetralin system. This work has resulted in a ranking of the minerals and identification of a mineral component common to the more reactive minerals. The results from this phase of the program will be presented.

Gangwer, T. Hydrogen Transfer Mechanisms Relevant to Coal Liquefaction. Informal presentation at Mobil Research & Development Corp., Princeton, New Jersey, December 15, 1978.

Program: Chemistry and Physics of Coal Utilization

Sponsor: DOE - Office of Basic Energy Sciences,
Chemical Sciences Division

HYDROGEN TRANSFER CATALYTIC ACTIVITY OF MINERALS COMMON TO COAL

BNL - 25235

T. Gangwer and H. Prasad

Chemical Sciences Division

The hydrogenation/dehydrogenation catalytic activity of minerals commonly present in coal was investigated. The extent of reaction undergone by the model hydrogen transfer system tetralin/1,2 dihydronaphthalene/naphthalene at 400°C in the presence of these minerals was used to measure the catalytic activity. Changes in the organic and inorganic components were monitored using kinetic, spectroscopic and physical measurement (i.e., x-ray diffraction; BET) techniques.

For the four most active minerals, the order of catalytic activity per gram of mineral, for a given range of particle size, is limonites > pyrites > diaspore > magnetites. The pure chemical analog of the limonites, Fe_2O_3, was found to have catalytic activity comparable with the limonites. Heating the minerals at 400°C before running the reaction was found to decrease these catalytic activities despite the surface area increases resulting from the annealing process. The catalytic activity per unit area of mineral was determined and used as an index of the catalytic activity of the reactive sites for these heterogeneous systems. The order of decreasing site catalysis activity for the more active minerals is pyrites > magnetites > diaspore > limonites.

The observed mineral/chemical compound catalytic activities indicate that the more reactive mineral hydrogenation/dehydrogenation catalytic sites are comprised of iron compounds.

Gangwer, T. and Prasad, H. Hydrogen Transfer Catalytic Activity of Minerals Common to Coal. Presented at 13th Middle Atlantic Regional Meeting, West Long Branch, New Jersey, March 19-23, 1979; Fuel (submitted).

Program: Chemistry and Physics of Coal Utilization

Sponsor: DOE - Office of Basic Energy Sciences,
Chemical Sciences Division

THERMODYNAMICS OF LIQUID Ca-Ag AND Ca-In ALLOYS

BNL - 23661

J. Delcet and J. J. Egan

Chemical Sciences Division

Free energies of mixing have been determined for the liquid binary alloys Ca-Ag and Ca-In at 800°C using an emf technique employing CaF_2 as a solid electrolyte. Although partial electronic conduction exists under certain conditions in CaF_2, it was still found useful as an electrolyte to obtain thermodynamic data. Appropriate equations are presented. The entropy of mixing of Ca-In alloys is also given.

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

Program: High Temperature Chemistry

Sponsor: DOE - Office of Basic Energy Sciences,
Chemical Sciences Division

THERMODYNAMICS OF DILUTE TERNARY CALCIUM ALLOYS

BNL - 23809

J. Delcet and J. J. Egan

Chemical Sciences Division

The change in the relative excess partial free energies of Ca in the solvent metals Bi, In, and Zn with addition of Mg has been determined at 800°C by operating the cells

$$\underset{X_{Ca} = .075}{\text{Ca-Mg-Me}(\ell)} \;\Big|\; \text{CaF}_2(s) \;\Big|\; \underset{X_{Ca} = .075}{\text{Ca-Me}(\ell)}$$

where the mole fraction of Mg was varied from 0.02 to 0.08.

Results agreed with those predicted by the equation

$$\frac{\partial G^E_{Ca}}{\partial X_{Mg}} = \frac{\partial G^E_{Mg}}{\partial X_{Ca}} \cong \pm \left[\frac{\partial G^E_{Ca}}{\partial X_{Ca}} \; \frac{\partial G^E_{Mg}}{\partial X_{Mg}} \right]^{\frac{1}{2}} \quad \begin{matrix} X_{Ca} \to 0 \\ X_{Ca} \to 0 \end{matrix}$$

which gives the behavior of the excess free energies of the dilute ternary systems if the behavior of the binary systems are known. Further, this equation was derived by Wagner on the basis that the Fermi energy of electrons is the determining factor in deviations from ideality. Results thus lend support to the idea that extreme non-ideality in alloys of Ca and Mg with Bi, In, and Zn is predominantly influenced by the electronic constitution.

Delcet, J. and Egan, J. J. Thermodynamics of Dilute Ternary Ca Alloys. Met. Trans. B (submitted).

Program: High Temperature Chemistry

Sponsor: DOE - Office of Basic Energy Sciences,
Chemical Sciences Division

ELECTRONIC CONDUCTION IN MOLTEN POTASSIUM CHLORIDE

BNL - 25368

R. E. Davis, R. J. Heus and J. J. Egan

Chemical Sciences Division

The Wagner-Hebb polarization technique, usually applied to solids, has been employed to measure electronic conductivity in molten KCl. Steady-state currents were measured at various applied voltages for the cell

$$\mathrm{Ta(s)} \;\big|\; \mathrm{KCl}(\ell) \;\big|\; \mathrm{K\text{-}Bi}(\ell)$$

Results showed the electronic conductivity to be proportional to the activity of K in KCl at temperatures between 800°C and 860°C and for activities of potassium less than 0.02. The apparent mobility and diffusion coefficient of electrons are reported as well as the activity coefficient of K in KCl and the transference number of ions.

Davis, R. E., Heus, R. J., and Egan, J. J. Electronic Conduction in Molten Potassium Chloride. Presented at Electrochemical Society Meeting, Pittsburgh, Pa., October 1978; J. Electrochem. Soc. (submitted).

Program: High Temperature Chemistry

Sponsor: DOE - Office of Basic Energy Sciences,
Chemical Sciences Division

THE FREE ENERGY OF FORMATION OF CaC_2

BNL - 25520

J. Delcet and J. J. Egan

Chemical Sciences Division

The free energy of formation of solid CaC_2 was determined at temperatures between 700°C and 800°C by measuring the emf of the cell

$$C(s),\ CaC_2(s)\ |\ CaF_2(s)\ |\ \underset{x_{Ca}\,=\,0.10}{Ca\text{-}Bi(\ell)}$$

At 800°C, the free energy was found to be

$$\Delta G_f^o = -95{,}630\ \text{kJ mol}^{-1}$$

Delcet, J. and Egan, J. J. The Free Energy of Formation of CaC_2. J. Chem. Thermodynamics (submitted).

Program: High Temperature Chemistry

Sponsor: DOE - Office of Basic Energy Sciences,
Chemical Sciences Division

EQUILIBRIUM THEORY OF ISOTOPE SEPARATION VIA HEATLESS ADSORPTION

BNL - 24252

F. B. Hill, Y. W. Wong and Y. N. Chan

Chemical Sciences Division

A theory of equilibrium heatless adsorption was developed for separation of two-component isotope mixtures. It was assumed that both components are adsorbed and obey a linear distribution law with one component present at trace levels. Calculations are presented on the performance of a single stage as a function of separation factor, pressure ratio and other operating parameters. Conditions for the complete removal of the more strongly adsorbed component from the product stream are also given. Features discussed include the critical purge-to-feed ratio, enrichment in the purge steam, and transient behavior of the columns.

Hill, F. B., Wong, Y. W., and Chan, Y. N. Equilibrium Theory of Isotope Separation Via Heatless Adsorption. Presented at AIChE 71st Annual Meeting, Miami Beach, Florida, November 12-16, 1978.

Program: Cyclic Separations Process Research

Sponsor: DOE - Office of Basic Energy Sciences,
Chemical Sciences Divison

EQUILIBRIUM AND KINETICS STUDIES OF HYDROGEN ISOTOPE EXCHANGE ON VANADIUM HYDRIDE

BNL - 24638

Y. W. Wong and F. B. Hill

Chemical Sciences Division

Chromatography experiments and pressure-composition isotherm measurements were carried out on the vanadium-hydrogen system in order to obtain an understanding of the equilibrium and kinetic factors affecting hydrogen isotope exchange. Analysis of the results yielded values of the hydrogen equilibrium distribution coefficient, the tritium-protium separation factor, the rate of the gas-solid exchange reaction, and the axial dispersion coefficient.

Wong, Y. W. and Hill, F. B. Equilibrium and Kinetics Studies of Hydrogen Isotope Exchange on Vanadium Hydride. A.I.Ch.E. Journal (submitted).

Program: Cyclic Separations Process Research

Sponsor: DOE - Office of Basic Energy Sciences,
Chemical Sciences Division

TRITIUM REMOVAL USING VANADIUM HYDRIDE

BNL - 24659

F. B. Hill, Y. W. Wong, and Y. N. Chan

Chemical Sciences Division

The results of an initial examination of the feasibility of separation of tritium from gaseous protium-tritium mixtures using vanadium hydride in cyclic processes is reported. Interest was drawn to the vanadium-hydrogen system because of the so-called inverse isotope effect exhibited by this system. Thus the tritide is more stable than the protide, a fact which makes the system attractive for revoval of tritium from a mixture in which the light isotope predominates. The initial results of three phases of the research program are reported, dealing with studies of the equilibrium and kinetics properties of isotope exchange, development of an equilibrium theory of isotope separation via heatless adsorption, and experiments on the performance of a single heatless adsorption stage.

In the equilibrium and kinetics studies, measurements were made of pressure-composition isotherms, the HT-H_2 separation factors and rates of HT-H_2 exchange. This information was used to evaluate constants in the theory and to understand the performance of the heatless adsorption experiments.

A recently developed equilibrium theory of heatless adsorption was applied to the HT-H_2 separation using vanadium hydride. Using the theory it was predicted that no separation would occur by pressure cycling wholly within the β phase but that separation would occur by cycling between the β and γ phases and using high purge-to-feed ratios.

Heatless adsorption experiments conducted within the β phase led to inverse separations rather than no separation. A kinetic isotope effect may be responsible. Cycling between the β and γ phases led to separation but not to the predicted complete removal of HT from the product stream, possibly because of finite rates of exchange.

Further experimental and theoretical work is suggested which may ultimately make possible assessment of the feasibility and practicability of hydrogen isotope separation by this approach.

Hill, F. B., Wong, Y. W., and Chan, Y. N. Tritium Removal Using Vanadium Hydride. Presented at Fifteenth D.O.E. Nuclear Air Cleaning Conference, Boston, Mass., August 1978.

Program: Cyclic Separations Process Research

Sponsor: DOE - Office of Basic Energy Sciences,
Chemical Sciences Division

DYNAMICS OF BUBBLES AND ENTRAINED PARTICLES IN A ROTATING FLUIDIZED BED

BNL - 24881

Rene Chevray, Yau Nam I. Chan, and Frank B. Hill

Chemical Sciences Division

Equations for the motion of bubbles and entrained particles in the rotating fluidized bed are presented and solved for a bed with a vertical axis. Illustrative trajectories are shown for a reference frame rotating with the bed.

At g-loadings of interest in rotating fluidized bed combustors the bubble velocity predicted via the Davies-Taylor approach agrees well with that obtained from solution of the complete three-dimensional force balance equations. However the latter equations are required to predict the deflection from a purely radial path arising from the action of the Coriolis force. The deflection is substantial in thick beds and should contribute significantly to good solids mixing in bubbling rotating systems.

Large particles ejected from the bed surface pass through the freeboard and return to the bed at points which are considerably removed from the point of ejection. This phenomenon also facilitates solids mixing. Particles of intermediate size are trapped in the freeboard region and sink slowly to the bottom of the vessel. Small particles follow a helical trajectory in the course of being elutriated from the bed. The rotating fluidized bed is shown to retain particles of at least the same size as those retained by the customary stationary fluidized bed but at a gas flowrate higher by a factor equal numerically to the g-loading.

Chevray, Rene, Chan, Yau Nam I., and Hill, Frank B. Dynamics of Bubbles and Entrained Particles in a Rotating Fluidized Bed. Presented at A.I.Ch.E. 86th National Meeting, Houston, Texas, April 1-5, 1979.

Program: Cyclic Separations Process Research

Sponsor: DOE - Office of Basic Energy Sciences,
Chemical Sciences Division

EQUILIBRIUM THEORY OF HEATLESS ADSORPTION

BNL - 25398

Yau Nam I. Chan, Frank B. Hill, and Yiu Wah Wong

Chemical Sciences Division

The equilibrium theory of heatless adsorption (Shendalman and Mitchell, 1972) was derived for the case of isothermal removal of a single adsorbable component, present at trace levels, from an inert carrier. The adsorbing component obeyed a linear distribution law. In the present work, a modification is made in the calculation of sorbate uptake in the pressurization step of the process, thereby rendering material balances for all steps in the process exact.

The modified theory is presented and extended to the case of the two component system in which both components are adsorbable. The equations describing the two situations are identical except for the interpretation of the parameter, β. For the inert major component case, β is the equilibrium fraction of the trace component in the gas. For an adsorbing major component, it is the ratio of the equilibrium capacity of the column for the major component relative to that of the minor. In the situation where both components are strongly adsorbable, β becomes the reciprocal of the separation factor of the trace component relative to the major component.

A survey was made of the predictions of the corrected theory. Calculations were made of the steady state performance of a single heatless adsorption stage when operating at the condition of complete removal of the trace component from the product stream. Quantities calculated included the critical purge to feed ratio, enrichments in the purge and in the blowdown gas, and overall enrichment.

Operation at the critical purge to feed ratio for perfect cleanup and the shortest column length corresponds to the condition of maximum sorbent utilization, providing an upper bound on the performance of the column. The overall enrichment increases with pressure ratio and decreases with β. It is dominated by the enrichment in the purge stream for small values of β. At a purge to feed ratio greater than the critical, the overall enrichment is diminished and exhibits a maximum with respect to pressure ratio. For separation factors less than unity, as expected, only modest depletion of the trace component in the product stream is found, and this depletion is relatively insensitive to pressure ratio. From transient calculations, the number of cycles required to reach steady state increases with pressure ratio.

Chan, Yau Nam I., Hill, Frank B., and Wong, Yiu Wah. Equilibrium Theory of Heatless Adsorption. Presented at A.I.Ch.E. 86th National Meeting, Houston, Texas, April 1-5, 1979.

Program: Cyclic Separations Process Research

Sponsor: DOE - Office of Basic Energy Sciences,
Chemical Sciences Division

TRACE ELEMENT ANALYSIS BY SYNCHROTRON RADIATION INDUCED X-RAY FLUORESCENCE

BNL - 25262

B. M. Gordon

Chemical Sciences Division

The merits of using X rays produced in an electron storage ring (synchrotron radiation) as the energy source in the application of x-ray fluorescence to multi-elemental trace analysis is discussed. Among the properties making synchrotron produced X rays particularly useful are its polarization, high intensity and tunability from a continuous energy spectrum. Sensitivity calculations are presented to illustrate the capabilities of the technique. Also, the high intensity synchrotron radiation can provide chemical speciation information for elements at the parts per million level. Preliminary plans for microprobe analysis of one micron resolution at the Brookhaven National Synchrotron Light Source are presented. Plans for operation of the project as a national users facility are also discussed.

Gordon, B. M. Trace Element Analysis by Synchrotron Radiation Induced X-ray Fluorescence. Presented at Second International Association of Bioinorganic Scientists Conference on Inorganic and Nutritional Aspects of Cancer, La Jolla, California, January 3-5, 1979.

Program: Trace Element Analysis Using Synchrotron Radiation

Sponsor: DOE - Office of Basic Energy Sciences,
Chemical Sciences Division

ANNUAL SUMMARY OF PROGRAMS IN ENERGY SCIENCES

BNL - 50795

D. J. Metz, Editor

Chemical Sciences Division

An overview of the programs in the Energy Sciences area of the Department of Energy and Environment is presented. The objective and scope of each current program is described, and summaries of significant accomplishments for CY 1977 and associated publications are given. The principal activities planned for CY 1978 are also described. New initiatives are listed.

BNL Progress Report

Program: Energy Sciences Programs of DEE

Sponsor: DOE - Office of Basic Energy Sciences,
Chemical Sciences Division

RADIATION EFFECTS OF ION EXCHANGE MATERIALS

BNL - 24639

T. E. Gangwer and K. K. S. Pillay

Chemical Sciences Division

An extensive literature survey was undertaken to examine the available data on radiation damages to ion exchange materials used in the nuclear process industry. Some of the important parameters useful in characterizing the effects of radiation on ion exchange resins have been compiled and the general trends in radiation effects on ion exchange resins have been summarized. In compiling the diverse types of experimental parameters and results, an effort was made to present the available data in a format that would allow for the intercomparison of radiation effects on different types of ion exchange materials under a variety of irradiation conditions. The deficiencies in the present knowledge on the radiation effects on ion exchange resins and the limitations of these data for generating quantitative predictive modelling are discussed.

Gangwer, T. E. and Pillay, K. K. S. Radiation Effects on Ion Exchange Materials. Third Annual Workshop on Actinide Removal, Idaho Falls, Idaho, June 1 and 2, 1978.

Program: Union Carbide Corp. (Oak Ridge National Lab.)

Sponsor: DOE - Office of Basic Energy Sciences,
Chemical Sciences Division

RADIATION EFFECTS ON ION EXCHANGE MATERIALS

BNL - 50781

T. E. Gangwer, M. Goldstein and K. K. S. Pillay

Chemical Sciences Division

An extensive literature review and data compilation has been completed on the radiation-damage of ion exchange resins. The primary goal of the study has been to review the available literature on ion exchange materials used in, as well as those with potential for use in, the nuclear fuel and waste reprocessing areas. The physical and chemical properties of ion exchangers are reviewed. Experimental parameters useful in characterizing the effects of radiation on synthetic ion exchange resins are identified or defined. In compiling the diverse types of data, an effort was made to present the experimental data or experimentally based parameters in a format that would be useful for intercomparing radiation effects on resins. When subject to radiation there are various general trends or qualitative effects displayed by the different types of resins. These radiation-trends and effects have been formulated into qualitative statements. The present day level of understanding of the behavior of resins under ionizing radiation is too limited to justify quantitative predictive modeling. The limitations and deficiencies of the literature are discussed and the experimentation needed to achieve quantitative modeling are outlined.

BNL Topical Report

Program: Union Carbide Corp. (Oak Ridge National Lab.)

Sponsor: DOE - Office of Basic Energy Sciences,
Chemical Sciences Division

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METALLURGY AND
MATERIALS SCIENCE DIVISION

EFFECT OF NEUTRON IRRADIATION ON SINGLE CRYSTAL V_3Si: HEAT CAPACITY AND RESISTIVITY

BNL - 23725

R. Viswanathan and R. Caton

Metallurgy and Materials Science Division

We have measured the heat capacity and resistivity of a V_3Si single crystal as a function of neutron irradiation up to a fluence of 22.2×10^{18} n/cm^2. The structural transformation was found to be extremely sensitive to very low level irradiations ($\sim .25 \times 10^{18}$ n/cm^2) whereas the superconducting transition temperature, T_c, was not affected up to $\sim 3 \times 10^{18}$ n/cm^2. The residual resistivity showed minor variations up to $\sim 3 \times 10^{18}$ n/cm^2 and started to change appreciably beyond that fluence. The electronic heat capacity coefficient and hence the density of states at the Fermi level was found to be considerably affected for <u>all</u> fluences. Further there is some evidence for the inhomogeneous nature of the irradiated state.

Viswanathan, R. and Caton, R. Effect of Neutron Irradiation on Single Crystal V_3Si: Heat Capacity and Resistivity. Phys. Rev. B. 18, pp. 15-21 (1978).

Program: Relationship between Properties and Structures

Sponsor: DOE - Office of Basic Energy Sciences,
Materials Sciences Division

THE DEPENDENCE OF THE SUPERCONDUCTING TRANSITION TEMPERATURE ON SILICON CONCENTRATION IN THE NbAlSi TERNARY SYSTEM

BNL - 23790

R. Caton and A. R. Sweedler

Metallurgy and Materials Science Division

We have prepared NbAlSi ternary alloys with up to 15 a/o Si in the A15 phase by rapid quenching from temperatures on the order of 2000°C and above. The superconducting transition temperature, T_c, lattice parameter, a_o, and composition for these alloys have been determined. X-ray diffractometer scans and metallography were also used to characterize the samples. No increase in T_c greater than a few tenths of a degree Kelvin was observed as the Si concentration was increased. However, large decreases in T_c with Si concentration were observed. These decreases are most likely associated with compositional and/or anti-site disorder, and correction for compositional disorder still indicates T_c decreases with increasing Si concentration beyond a few at.% Si.

Caton, R. and Sweedler, A. R. The Dependence of the Superconducting Transition Temperature on Silicon Concentration in the NbAlSi Ternary System. J. of Less Common Metals, 60, p. 91 (1978).

Program: Relationship between Properties and Structures

Sponsor: DOE - Office of Basic Energy Sciences,
Materials Sciences Division

COMMENT ON THE PAPER "EXAFS MEASUREMENTS ON Nb_3Ge THIN FILMS"

BNL - 23899

C. S. Pande and R. Viswanathan

Metallurgy and Materials Science Division

Brown, et al. has reported recently that Nb_3Ge specimens showing superconducting transition temperatures less than the maximum possible value contain a 'quasi-amorphous phase'. We discuss the possibility that the lower values of T_c of these specimens may be accounted for by the proximity effect due to these quasi-amorphous regions.

Pande, C. S. and Viswanathan, R. Comment on the Paper "EXAFS Measurements on Nb_3Ge Thin Films". Sol. State Comm. 26, pp. 893-895 (1978).

Program: Relationship between Properties and Structures

Sponsor: DOE - Office of Basic Energy Sciences,
Materials Sciences Division

THE NATURE OF THE DEFECTS IN IRRADIATED A15 COMPOUNDS

BNL - 24154

C. S. Pande and R. Viswanathan

Metallurgy and Materials Science Division

From transmission electron microscopy and heat capacity measurements radiation induced damage in A15 compounds was found to be inhomogeneous, consisting of small disordered regions in an ordered matrix. Some consequences of this result are discussed.

Pande, C. S. and Viswanathan, R. The Nature of the Defects in Irradiated A15 Compounds. Published in proceedings of L.T. 15, Journal de Physique, 39, C6-389 (1978).

Program: Relationship between Properties and Structures

Sponsor: DOE - Office of Basic Energy Sciences,
Materials Sciences Division

SUPERCONDUCTING TRANSITION TEMPERATURE WIDTHS IN NEUTRON-IRRADIATED SINGLE CRYSTAL V_3Si

BNL - 24163

R. Viswanathan, R. Caton, and C. S. Pande

Metallurgy and Materials Science Division

Superconducting transition temperature T_c, and its width ΔT_c were measured in neutron ($E>1$ MeV) irradiated V_3Si as a function of fluence ϕt using (a) heat capacity and (b) resistive measurements. It is found that the two measurements for T_c and ΔT_c do not give identical results. However in both cases ΔT_c increases with fluence indicating the inhomogeneous nature of the damage.

Viswanathan, R., Caton, R., and Pande, C. S. Superconducting Transition Temperature Widths in Neutron-Irradiated Single Crystal V_3Si. Phys. Rev. Lett. 41, pp. 906-910 (1978).

Program: Relationship between Properties and Structures

Sponsor: DOE - Office of Basic Energy Sciences,
Materials Sciences Division

NORMAL STATE RESISTIVITY OF SINGLE CRYSTALLINE V_3Si AS A FUNCTION OF NEUTRON IRRADIATION

BNL - 24251

R. Caton and R. Viswanathan

Metallurgy and Materials Science Division

Analysis of the normal state resistivity of a neutron damaged single crystal of V_3Si shows two different regions of behavior: one for $T_c \geq 10K$ and the other for $T_c \leq 10K$.

Caton, R. and Viswanathan, R. Normal State Resistivity of Single Crystalline V_3Si as a Function of Neutron Irradiation. Presented at International Conference on Low Temperature Physics, Grenoble, France, Aug. 23-29, 1978.

Program: Relationship between Properties and Structures

Sponsor: DOE - Office of Basic Energy Sciences,
Materials Sciences Division

TRANSMISSION ELECTRON MICROSCOPY OF RADIATION DAMAGE IN Nb_3Sn

BNL - 24304

C. S. Pande

Metallurgy and Materials Science Division

The nature of the defect or defect complexes produced in superconducting compound Nb_3Sn by high energy ($E \geq 1$ MeV) neutron irradiation is studied by transmission electron microscopy. The damage appears to be primarily in the form of highly disordered regions of size 2 to 6 nm in a much less disordered matrix. Both the ordered matrix and the disordered regions essentially retain A15 structure. Using superlattice and fundamental reflections it is shown that the disordered regions contain a high density of antisite defects as well as associated strain fields.

Pande, C. S. Transmission Electron Microscopy of Radiation Damage in Nb_3Sn. Physica Status Solidi, April 16, 1979 (in press).

Program: Relationship between Properties and Structures

Sponsor: DOE - Office of Basic Energy Sciences,
Materials Sciences Division

SOME PROBLEMS IN THE "T_c Vs N(0) CORRELATION" IN NEUTRON IRRADIATED V_3Si

BNL - 24308

R. Viswanathan, C. S. Pande, R. Caton, and D. O. Welch

Metallurgy and Materials Science Division

Heat capacity measurements on neutron irradiated V_3Si show that the initial drop in the bare density of states at the Fermi level N(0) is <u>not</u> accompanied by corresponding changes in the superconducting transition temperature T_c. This is discussed in the context of various models for the effect of lattice defects on the superconducting properties of A15 compounds. It is suggested that the inhomogeneous nature of neutron damage may be significant in understanding these results.

Program: Relationship between Properties and Structures

Sponsor: DOE - Office of Basic Energy Sciences,
Materials Sciences Division

THE PROPERTIES OF SUPERCONDUCTING A15 Nb_3Si

BNL - 24424

David Dew-Hughes

Metallurgy and Materials Science Division

Superconducting A15 Nb_3Si has been made by the explosive compression of the high temperature, equilibrium, tetragonal Ti_3P phase, confirming the work of Pan et al. This material has a broad superconducting transition with an onset T_c of ~18K and a midpoint ~16K. X-ray diffraction data are consistent with a highly disordered A15 structure with a spread of lattice parameter from ~5.12-5.17Å. Preliminary indications suggest that the upper critical field at 4.2K may be in excess of 40 tesla. Measurements of H_{c2} as a function of temperature and low temperature specific heat of this material are underway and will be reported. Studies of radiation damage and annealing behavior are also being made. Prospects for higher critical temperatures and improved materials will be discussed.

Dew-Hughes, David. The Properties of Superconducting A15 Nb_3Si. IEEE Trans. on Mag., MAC-15, p. 490 (1979).

Program: Relationship between Properties and Structures

Sponsor: DOE - Office of Basic Energy Sciences,
Materials Sciences Division

SCATTERING OF X-RAYS IN IRRADIATED A15 COMPOUNDS

BNL - 24469

C. S. Pande and R. Viswanathan

Metallurgy and Materials Science Division

Recent transmission electron microscopy of neutron irradiated Nb_3Sn showed that the irradiation primarily produces small coherent disordered regions in a much less disordered matrix. This paper examines the x-ray scattering for such a system within the framework of the kinematic theory of x-ray diffraction. It is shown that the x-ray observations in irradiated A15 compounds viz (a) uniform lattice expansion, (b) no significant change in x-ray line widths, and (c) a weakening of both fundamental and superlattice line intensities on irradiation, are consistent with the electron microscopic observations.

Pande, C. S. and Viswanathan, R. Scattering of X-Rays in Irradiated A15 Compounds. J. of Less Common Metals 62, pp. 119-126 (1978).

Program: Relationship between Properties and Structures

Sponsor: DOE - Office of Basic Energy Sciences,
Materials Sciences Division

FORMATION OF SUPERCONDUCTING Nb_3Si BY EXPLOSIVE COMPRESSION

BNL - 24546

D. Dew-Hughes and V. D. Linse

Metallurgy and Materials Science Division

The claim that the high-temperature equilibrium tetragonal Nb_3Si phase can be transformed, by explosive compression, into a superconducting phase, has been confirmed. After being subjected to shock compression with peak pressure close to 1 Mbar, the resulting material is superconducting, with an onset T_c of 18 K. The structure of this superconducting phase is ambiguous, but it could have the A15 structure with a lattice parameter of 5.12Å.

Dew-Hughes and Linse, V. D. Formation of Superconducting Nb_3Si by Explosive Compression. J. of Appl. Phys., 1979, (to be published).

Program: Relationship between Properties and Structures

Sponsor: DOE - Office of Basic Energy Sciences,
Materials Sciences Division

THE EFFECT OF HYDROGEN ON THE MECHANICAL PROPERTIES OF Fe WHISKERS

BNL - 24574

K. S. Lee and D. Dew-Hughes

Metallurgy and Materials Science Division

In an attempt to gain a fundamental understanding of the mechanism of hydrogen assisted cracking, the effect of hydrogen upon the tensile properties of pure iron whiskers was studied. The presence of hydrogen, introduced cathodically either by precharging or by charging during the test, was found to have no discernible influence upon the elastic modulus, yield point or ultimate tensile strength as determined in a simple tension test. Nor did the presence of hydrogen have any effect upon rates of stress-relaxation. Very occasionally in a stress-relaxation test a charged specimen would show delayed fracture; this never happened with an uncharged specimen. Examination of the fractured surfaces showed that, in all cases, fracture was fully ductile, giving an ideal, chisel point fracture.

The absence of any effect of hydrogen is presumed to result from the purity of whiskers, which, because they are grown by reduction of iron chloride vapor, probably contain very low levels of carbon and nitrogen. Hydrogen assisted cracking in steel has been shown to be a function of material purity.

Lee, K. S. and Dew-Hughes, D. The Effect of Hydrogen on the Mechanical Properties of Fe Whiskers. Presented at TMS-AIME Fall Meeting, St. Louis, MO, Oct. 15-19, 1978.

Program: Relationship between Properties and Structures

Sponsor: DOE - Office of Basic Energy Sciences,
Materials Sciences Division

A THEORETICAL ESTIMATE OF THE STRAIN-DEPENDENT ELASTIC DIPOLE TENSOR FOR INTERSTITIAL IMPURITIES IN B.C.C. METALS AND OF THE STRENGTH OF THE NON-LINEAR SNOEK EFFECT

BNL - 24588

D. S. Richter and D. O. Welch

Metallurgy and Materials Science Division

The strain-dependent elastic dipole tensor was calculated with a microscopic model based on pairwise interatomic interactions for several interstitial impurities in b.c.c. hosts: C in Fe, N in V, N in Nb, and O in Nb. Calculated tensor components at zero-strain agree reasonably well with experimental values. The calculated strain dependence of the dipole tensor was used to predict the relaxation of third-order elastic constants to be expected from the non-linear anelastic analog of the Snoek effect. The results suggest that such an effect should be experimentally observable and should provide additional information about impurity-host interatomic forces.

Richter, D. S. and Welch, D. O. A Theoretical Estimate of the Strain-Dependent Elastic Dipole Tensor for Interstitial Impurities in B.C.C. Metals and of the Strength of the Non-Linear Snoek Effect. Scripta Metallurgica 12, pp. 831-835 (1978).

Program: Relationship between Properties and Structures

Sponsor: DOE - Office of Basic Energy Sciences,
Materials Sciences Division

THE LOW TEMPERATURE MECHANICAL PROPERTIES OF CAST DUPLEX STAINLESS STEELS

BNL - 24833

K. S. Lee and D. Dew-Hughes

Metallurgy and Materials Science Division

Cast stainless steels are being proposed for a variety of structural applications in cryogenic installations. In particular centrifugally cast tubes will be used to contain the superconducting magnets for ISABELLE, the new 400 GeV Proton Intersecting Storage Ring device now under construction at BNL. Depending upon chemical composition and cooling rate, cast austenitic Fe-Cr-Ni (CF grade) stainless steel may contain considerable amount of δ-ferrite. Consequently the effect of δ-ferrite on the mechanical properties and stability against transformation to martensite in these steels at low temperatures is of urgent practical interest.

The mechanical properties, tensile strength and Charpy impact values, have been measured over the temperature range 300K-4.2K in samples of centrifugally cast CF8 steels with differing ferrite contents. The presence of adequate amounts of ferrite increases the tensile strength, without sacrificing ductility or impact strength, over this temperature range. The stability of these steels in regard to martensite formation has been examined over the same temperature range by both optical microscopy and magnetic measurements. Cast duplex structures are more stable than wrought stainless steel of the same chemical composition, due to segregation of the austenite-stabilizing elements enriching the austenite phase during solidification. Optical and scanning electron microscopy have been used to study the effect of both δ-ferrite and stress-induced martensite on the fracture mode and crack paths over the same temperature

Lee, K. S. and Dew-Hughes, D. The Low Temperature Mechanical Properties of Cast Duplex Stainless Steels. Presented at the Annual TMS-AIME Meeting, New Orleans, LA, Feb. 18-22, 1979, (to be published).

Program: Relationship between Properties and Structures

Sponsor: DOE - Office of Basic Energy Sciences,
Materials Sciences Division

ALTERATION BY ELASTIC STRAIN OF THE SUPERCONDUCTING TRANSITION TEMPERATURES OF Nb_3Sn, V_3Ge, and V_3Si IN "BRONZE PROCESSED" COMPOSITE WIRES

BNL - 25362

K. Aihara, D. O. Welch, M. Suenaga, and T. S. Luhman

Metallurgy and Materials Science Division

A residual compressive strain in the A15 compound is intrinsic to composite superconductors produced by the "bronze process", due to differential thermal contraction between the bronze matrix and the core. The strain magnitude can be systematically varied by etching away the bronze matrix or by externally applying strain to the composite. These techniques have been used to study the strain dependence of T_c in several A15 compounds. Results obtained by etching agree with those obtained with external strain. T_c varies essentially quadratically with strain. 1% strain depressed T_c by 1.8K in Nb_3Sn and increases T_c by 1.3K in V_3Ge. The magnitude of the depression of T_c in V_3Si is comparable to that in Nb_3Sn while the depression in V_3Ga is substantially smaller.

Aihara, K., Welch, D. O., Suenaga, M., and Luhman, T. S. Alteration by Elastic Strain of the Superconducting Transition Temperatures of Nb_3Sn, V_3Ge, and V_3Si in "Bronze Processed" Composite Wires. To be presented at the 1979 March Meeting of the American Physical Society, Chicago, IL, March 19-23, 1979. Bull. Am. Phys. Soc. 24, p. 456 (1979).

Program: Relationship between Properties and Structures

Sponsor: DOE - Office of Basic Energy Sciences
Materials Sciences Division

SOFTENING OF YOUNG'S MODULUS IN POLYCRYSTALLINE Nb_3Sn

BNL - 25363

D. O. Welch, J. F. Bussiere, and M. Suenaga

Metallurgy and Materials Sciences Division

Ultrasonic measurements[1] show that the shear modulus $(C_{11}-C_{12})/2$ softens dramatically as single crystals of Nb_3Sn approach the martensitic transition near 50K. It is expected that Young's modulus of polycrystals will also soften, but previous ultrasonic measurements,[2] which suffer from severe damping, fail to show the expected effect. We have measured Young's modulus of polycrystalline Nb_3Sn between 4.2K and 300K by static beam deflection methods, and observe marked softening. A value of $15\pm1\times10^{11}$ dyne cm^{-2} was obtained at 300K by the deflection of thin Nb_3Sn-Nb-Nb_3Sn composite strips by external stress. The variation of the modulus with T was obtained from the change in the radius of curvature of internally stressed Nb_3Sn-Nb composite strips. (This method is made possible by the perfect match between the thermal expansion coefficients of Nb and Nb_3Sn.) The modulus is found to be proportional to lnT between 50K and 300K and is temperature independent below the superconducting T_c, resulting in a decrease by a factor of 2.7 between 300K and 18K. This variation is in reasonable agreement with that obtained by a polycrystalline average of experimental values of single crystal elastic constants,[1] although our value at 300K is slightly higher than that obtained by averaging, 13.5×10^{11} dyne cm^{-2}.

Welch, D. O., Bussiere, J. F., and Suenaga, M. Softening of Young's Modulus in Polycrystalline Nb_3Sn. To be presented at the International Conference on Martensitic Transformations (ICOMAT-79), Cambridge, MA, June 24-29, 1979.

Program: Relationship between Properties and Structures

Sponsor: DOE - Office of Basic Energy Sciences,
Materials Sciences Division

SHELL MODEL CALCULATION OF THE IONIZATION POTENTIALS OF ALKALI HALIDES

BNL - 25365

D. O. Welch, O. W. Lazereth, and G. J. Dienes

Metallurgy and Materials Sciences Division

A shell model calculation, previously used to investigate the characteristics of alkali halide molecules and small aggregates,[1] was extended to the study of the halide and metal ionization potentials of these molecules and crystals. Ionization potentials were calculated via the Born-Haber cycle applied to the binding energy of the ionized system relative to the ground state. The total ionization energy is a smooth function of aggregate size, converging rapidly to the infinite crystal value. However, the partition of the ionization energy into Coulomb and polarization contributions varies strongly with size. Results will be compared with the meager experimental data.

Welch, D. O., Lazereth, O. W., and Dienes, G. J. Shell Model Calculation of the Ionization Potentials of Alkali Halides. To be presented at the 1979 March Meeting of the American Physical Society, Chicago, IL, March 19-23, 1979. Bull. Am. Phys. Soc. 24, p. 404 (1979).

Program: Relationship between Properties and Structures

Sponsor: DOE - Office of Basic Energy Sciences,
Materials Sciences Division

FABRICATION OF SUPERCONDUCTING MATERIALS FOR LARGE MAGNETIC DEVICES

BNL - 25369

M. Suenaga and W. B. Sampson

Metallurgy and Materials Science Division

Due to the increased interest in the use of superconductors for large magnetic devices such as fusion power reactors and high energy particle accelerators, fabrication techniques for multifilamentary superconducting composites have progressed considerably in the last few years. Since such developments have been largely confined to improved processing methods for A15 type superconductors, this review will concentrate on the development of multifilamentary Nb_3Sn and V_3Ga conductors.

The metallurgical principles of formation of Nb_3Sn [V_3Ga] at the Nb-(Cu-Sn) [V-(Cu-Ga)] interface by a solid state diffusion process is first described. Then, each processing method for multifilamentary composites is critically reviewed pointing out its advantages and disadvantages in possible large scale production. The fabrication techniques fall into two categories; I) continuous filament processes which includes the so-called "bronze route", and external and internal Sn diffusion methods, II) multiply connected filament schemes which include the so-called Tsuei's or "in situ" wires and Sn infiltration processes. Since in many cases Cu stabilizers within the superconductors are desirable, the applicability and methods for simultaneous processing barriers to avoid Sn diffusion into the stabilizing copper are also discussed.

Superconducting properties, primarily the superconducting critical current density, J_c, at high magnetic fields, are compared for wires made by the above processes. Where it is possible, the differences in J_c are related to the different manufacturing methods. In addition, the behavior of these conductors under mechanical strain (in tension as well as bending), which is one of the most critical properties of these materials, is compared and discussed in terms of recent progress in understanding the degradation phenomenon. Finally, some important considerations for designing conductors for specific applications are pointed out. These include improvements in superconducting properties by alloying as well as the geometrical arrangements of the filaments to achieve the optimum performance under the restructions imposed by the magnet design.

Suenaga, M. and Sampson, W. B. Fabrication of Superconducting Materials for Large Magnetic Devices. To be presented at the Electrochemical Society Symposium, Boston, MA, May 6-11, 1979.

Program: Relationship between Properties and Structures

Sponsor: Office of Basic Energy Sciences,
Materials Science Division

A MEASUREMENT OF THE TEMPERATURE DEPENDENT YOUNG'S MODULUS OF POLYCRYSTALLINE Nb_3Sn

BNL - 25370

J. F. Bussiere, D. O. Welch, and M. Suenaga

Metallurgy and Materials Sciences Division

Young's modulus of polycrystalline Nb_3Sn was measured between 4.2K and 300K by static beam deflection methods. A value of $15 \pm 1 \times 10^{11}$ dyne cm^{-2} was obtained by the deflection of thin Nb_3Sn-Nb-Nb_3Sn composite strips by external stress. The variation of the modulus with T was obtained from the change in the radius of curvature of internally stressed Nb_3Sn-Nb composite strips. (This method is made possible by the perfect match between the thermal expansion coefficients of Nb and Nb_3Sn.) The modulus is found to be proportional to lnT between 50K and 300K and is temperature independent below the superconducting T_c, resulting in a decrease by a factor of 2.7 between 300K and 18K. This variation is in reasonable agreement with that obtained by a polycrystalline average of experimental values of single crystal elastic constants,[1] although our value at 300K is slightly higher than that obtained by averaging, 13.5×10^{11} dyne cm^{-2}.

Bussiere, J. F., Welch, D. O., and Suenaga, M. A Measurement of the Temperature Dependent Young's Modulus of Polycrystalline Nb_3Sn. Presented at the March Meeting of the American Physical Society, Chicago, IL, March 19-23, 1979. Bull. Am. Phys. Soc. 24, p. 425 (1979).

Program: Relationship between Properties and Structures

Sponsor: DOE - Office of Basic Energy Sciences,
Materials Sciences Division

SWELLING OF NEUTRON-IRRADIATED Mo and Mo-0.5 Ti BY MEANS OF POSITRON ANNIHILATION

BNL - 23768

C. L. Snead, Jr., K. G. Lynn, and A. N. Goland

Metallurgy and Materials Science Division

Molybdenum specimens have been irradiated in the EBR-II over a temperature range 425-1500°C and Mo-0.5 Ti specimens over the range 425-1050°C. The swelling as defined by the volume of the voids generated was investigated using both lifetime and Doppler-broadening positron annihilation measurements. Positron trapping at the radiation-induced microstructure (loops) is extracted from the data and is not included in the effects attributed to voids. In both materials a single swelling peak is indicated although a double peak spectrum cannot be absolutely ruled out. The Mo-0.5 Ti results are generally very similar to those in Mo (lifetime in a void is ~470 psec in both materials swelling peak at ~650°C). Differences in details will be discussed as will the effects of irradiation temperature on the relative contributions of both voids and microstructure to the positron trapping.

Snead, C. L., Jr., Lynn, K. G., and Goland, A. N. Swelling of Neutron-Irradiated Mo and Mo-0. 5 Ti by Means of Positron Annihilation. Presented at the March APS Meeting, Washington, DC, March 27-30, 1978.

Program: Radiation Damage

Sponsor: DOE - Office of Basic Energy Sciences,
Materials Sciences Division

NEUTRON-IRRADIATION EFFECTS IN THE PSEUDOBINARY COMPOUND $Nb_3(SnGa)$: CHANGES T_c, I_c, AND FLUX PINNING

BNL - 24282

C. L. Snead, Jr. and M. Suenaga

Matallurgy and Materials Science Division

Specimens of single-core wires of $Nb_3(SnGa)$ have been neutron irradiated at ~100°C to fluences of $2.6 \times 10^{19} n/cm^2$ ($E > 1.0$ MeV). Measurements of I_c at 4.2K in transverse magnetic fields to 22T, and measurements of T_c were made. The interest in this material (~1 at.% Ga in the Nb_3Sn layer made by the "bronze process") stems from the greater critical-properties' values (T_c=17.4K, H_{c2}~ 22.5T) relative to those of Nb_3Sn. Results are given for two different specimen reaction temperatures, 700 and 750°C. Increases in I_c for low fluence ($< 3 \times 10^{18} n/cm^2$) irradiations similar to those observed for Nb_3Sn were observed, but with greater relative increases for the specimens (750°C) that had the <u>lower</u> initial current density. Decreases in I_c at higher fluences scaled with the measured decreases in T_c similar to behavior of Nb_3Sn. Increases of H_{c2} observed in Nb_3Sn in the low-dose regime were not found for these compounds. Indeed, the nonlinear behavior of plots of the pinning force F_p vs $h^{1/2}(1-h)^2$ where h is the reduced field suggests a limiting phenomenon in H_{c2}. Whether this is paramagnetic in nature is not at present known. When scaling is investigated in plots of F_p vs h, no peak shifts are observed following the first low dose of $\sim 5 \times 10^{16} n/cm^2$.

Snead, C. L., Jr. and Suenaga, M. Neutron-Irradiation Effects in the Pseudobinary Compound $Nb_3(SnGa)$: Changes T_c, I_c, and Flux Pinning. Presented at the 1978 Applied Superconductivity Conference, Pittsburgh, PA, September 25-28, 1978. IEEE Trans. on Mag., MAG-<u>15</u>, pp. 625-626 (1979).

Program: Radiation Damage

Sponsor: DOE - Office of Basic Energy Sciences,
Materisls Sciences Division

THE EFFECTS OF IRRADIATION ON SUPERCONDUCTING PROPERTIES OF CANDIDATE MAGNET CONDUCTORS

BNL - 24834

C. L. Snead, Jr. and M. Suenaga

Metallurgy and Materials Science Division

The response of critical properties of A15 [Nb_3Sn, V_3Ga, and $Nb_3(SnGa)$] and NbTi superconducting wires to radiation damage is reviewed. The mechanisms that are active in reducing the critical current, I_c, of NbTi in all dose regimes, and those active in changes in A15's (increases in I_c and the upper critical field, H_{c2}, at low fluences where critical temperature, T_c, is relatively unchanged, and decreases in I_c, H_{c2}, and T_c at high fluence) are discussed. Data which are obtained after reactor ambient-temperature neutron irradiation and low-temperature high-energy proton irradiations are included. In particular, the role of annealing following the various types of irradiation on the recovery of the irradiation-induced critical-property changes will be highlighted. Anneals up to room temperature of the helium-temperature-irradiated-specimens show significant recovery in I_c for NbTi. Small, dose-dependent recovery in I_c is seen in A15 specimens after low-temperature irradiation. However, anneals to temperatures significantly above the irradiation temperature (~100°C) are required for the high-fluence neutron-irradiated specimens to recover the T_c degradations to any appreciable degree. Some implications of the recovery in the superconducting properties after annealing related to the operation of a fusion-reactor magnet are then discussed.

Snead, C. L., Jr. and Suenaga, M. The Effects of Irradiation on Superconducting Properties of Candidate Magnet Conductors. Presented at First Topical Meeting on Fusion Reactor Materials, Miami Beach, FL, January 29-31, 1979.

Program: Radiation Damage

Sponsor: DOE - Office of Basic Energy Sciences,
Materials Sciences Division

USE OF POSITRONS IN THE STUDY OF VOIDS AND OTHER EXTENDED IRRADIATION-INDUCED DEFECTS

BNL - 25012

C. L. Snead, Jr.

Metallurgy and Materials Science Division

The techniques of positron annihilation have been applied to the study of extended defects resulting from, principally, neutron irradiation. These studies will be reviewed with the aim of (1) comparing void characteristics observed for both irradiations at elevated and lower temperature and subsequently annealed, (2) examining the rôle that dislocation loops play in the study of void properties, (3) and determining the applicablity and sensitivity of these techniques to the evaluation of swelling properties in irradiated metals. Since the presence of gases in the matrix is important to both void and bubble nucleation and growth, the work done on bubble formation and growth following gas injection will be discussed. The strengths and limitations of positron techniques in these studies will be presented.

Snead, C. L., Jr. Use of Positrons in the Study of Voids and Other Extended Irradiation-Induced Defects. Presented at Annual TMS-AIME Meeting, New Orleans, LA, Feb. 19-22, 1979.

Program: Radiation Damage

Sponsor: DOE-Office of Basic Energy Sciences,
Materials Sciences Division

DETERMINATION OF FORMATION AND BINDING ENERGIES FOR VACANCIES AND IMPURITIES IN Ni AND DILUTE Ni ALLOYS

BNL - 25079

C. L. Snead, Jr., K. G. Lynn, and K. Farrell

Metallurgy and Materials Science Division

Both lifetime and Doppler-broadening techniques have been employed in the study of pure nickel and twelve dilute (typically 1000 ppm) binary alloys of Ni. Lifetime results on pure Ni for temperatures from 4.2 to 1700K produce a value for the single-vacancy formation energy E^{1V} for pure Ni of 1.48 ± 0.05 eV. This value and the results of the Doppler-broadening studies agree with the results of Campbell et al.(1) For the lifetime measurements in Ni between 4.2 and 800K no evidence of effects due to volume expansion were found. A linearly increasing mean positron lifetime in the temperature range 800-1100K, prior to the onset of vacancy trapping, was observed as has been found in some other metals. The results of the single-vacancy--impurity binding-energy determination in the twelve dilute binary alloys will be presented. These will be discussed in terms of both size and valence effects of the alloying agents on the binding energies.

Snead, C. L., Jr., Lynn, K. G., and Farrell, K. Determination of Formation and Binding Energies for Vacancies and Impurities in Ni and Dilute Ni Alloys. Presented at 5th International Conference on Positron Annihilation, Lake Yamanaka, Japan, April 8-11, 1979.

Program: Radiation Damage

Sponsor: DOE - Office of Basic Energy Sciences
Materials Sciences Division

STRESS-INDUCED ENHANCEMENT OF T_c IN BRONZE-PROCESSED V_3Ge

BNL - 23723

J. F. Bussière, T. Onishi, D. O. Welch, and M. Suenaga

Metallurgy and Materials Science Division

Compressive stresses arising from differential contraction of the bronze matrix were found to cause an increase in the critical temperature, T_c, of bronze-processed V_3Ge. This unusual behavior for an A15 compound is found to be consistent with calculations based on Testardi's theory, although the enhancement of T_c appears to saturate at large residual strains.

Bussiere, J. F., Onishi, T., Welch, D. O., and Suenaga, M. Stress-Induced Enhancement of T_c in Bronze-Processed V3Ge. Appl. Phys. Lett. 32, p. 686 (1978).

Program: Superconducting Power Transmission Lines
Relationship between Properties and Structure

Sponsor: Electric Energy Systems Division/DOE
Materials Science Program/DOE

PROPERTIES OF PLASTIC TAPES FOR CRYOGENIC POWER CABLE INSULATION

BNL - 24309

A. C. Muller

Electrical Energy Systems Division

Specialized plastic tapes are under development as dielectric insulation for ac superconducting power transmission cables. Cable design requirements specify that candidate tapes must possess very high tensile moduli at 293K, be flexible at 6K, and experience a minimum amount of thermal expansion between 6K and 293K. High thermal conductivity and small dielectric loss at 6K are also required by design considerations. Most requirements may be satisfied with a biaxially-oriented, very-high-modulus, polypropylene film laminate. In particular, low temperature brittleness was eliminated with this design. Developmental work is also under way of a high-draw-ratio, ultra-high-modulus, polyethylene tape fabricated by a solid state extrusion process. Mechanical, thermal, and dielectric data taken at cryogenic temperatures will be discussed.

Muller, A. C. Properties of Plastic Tapes for Cryogenic Power Cable Insulation. To be published in Nonmetallic Materials and Composites at Low Temperatures, A. F. Clark, R. P. Reed, and G. Hartwig, Editors, pp. 339-363, Plenum Press, New York, 1979.

Program: Superconducting Power Transmission Lines

Sponsor: DOE - Office of Energy Technology,
Electrical Energy Systems Division

X-RAY ANALYSIS OF TRAPPING STRUCTURE IN LAPPED HIGH VOLTAGE UNDERGROUND POWER TRANSMISSION CABLES

BNL - 24989

A. C. Muller

Electrical Energy Systems Division

Brookhaven has developed a nondestructive method to study the mechanical structure of the insulation of lapped power cables both in the factory and in the field. The system employs a point source of soft x-rays and a closed circuit television. The electrical insulation of high voltage underground, pipe-type power cables is comprised of several hundred layers of porous kraft-paper tape impregnated with insulating oil. These, and other lapped cable designs, attain their maximum strengths when the tapes are applied in predetermined, regular patterns at set winding tensions. Alterations in the taping pattern can lower the electrical strength of a cable and reduce its life. A mobile version of the system has been used extensively in the field to examine cables that have experienced severe thermal and mechanical stresses.

Muller, A. C. X-Ray Analysis of Trapping Structure in Lapped High Voltage Underground Power Transmission Cables. Presented at the 1977 Winter Meeting of the IEEE Power Engineering Society, New York, January 1977 (Paper A77 108-3).

Program: Superconducting Power Transmission Lines

Sponsor: DOE - Office of Energy Technology,
Electrical Energy Systems Division

ELASTIC MODULUS OF POLYCRYSTALLINE Nb_3Sn BETWEEN 4.2 AND 300K

BNL - 24978

J. F. Bussière, D. O. Welch, and M. Suenaga

Metallurgy and Materials Science Division

Young's modulus for polycrystalline Nb_3Sn has been measured between 4.2 and 300K using an internally stressed bimetallic strip consisting of pure niobium and Nb_3Sn. The modulus is obtained by observing the radius of curvature of the strip as a function of temperature. Because of a perfect match between the thermal expression coefficients of Nb and Nb_3Sn, the radius of curvature can be directly related to changes of modulus of either the Nb or Nb_3Sn. Results indicate that the modulus of Nb_3Sn decreases by approximately a factor of two between 300 and 18K, and that no change occurs below the superconducting transition. Our measurements indicate a much larger change in modulus than previously observed for polycrystalline Nb_3Sn by ultrasonic techniques, but are in better agreement with polycrystalline averages based on ultrasonic data for single crystals.

Bussiere, J. F., Welch, D. O., and Suenaga, M. Elastic Modulus of Polycrystalline Nb_3Sn between 4.2 and 300K. Presented at Annual TMS-AIME Meeting, New Orleans, Feb. 18-22, 1979.

Programs: Relationship between Properties and Structures (and)
Superconducting Power Transmission Lines

Sponsors: DOE - Office of Basic Energy Sciences,
Materials Sciences Division (and)
DOE - Office of Energy Technology,
Electrical Energy Systems Division

HYDROGEN ABSORPTION IN THE NIOBIUM-VANADIUM SYSTEM

BNL - 24678

Michael A. Pick and David O. Welch

Metallurgy and Materials Science Division

The objective of the investigation is to understand the influence which substitutional additions have on metal-hydrogen systems. A generalization of the results should lead to an understanding of the influence of defects and impurities on hydrogen solubilities as well as phase transitions and deviations from Sievert's law. We have begun this study with an investigation of several properties of the niobium-vanadium-hydrogen system. In recent publications Matsumoto et al.(1) have claimed that substitutional vanadium atoms in niobium are strong local hydrogen "traps". We have calculated the effect such a binding would have on the phase diagram and the pressure-temperature-composition isotherms. The model is based on the long-range elastic hydrogen-hydrogen interaction as originally proposed by Alefeld.(2) A trapping of hydrogen at the substitutional vanadium sites will result in a characteristic change in the shape of the isotherms at low concentrations. Experimental data which we have gathered on the NbV-system shows a depression of the critical point as compared to pure niobium which can be interpreted as an increase in the terminal solubility. However, pressure-temperature-composition isotherms measured in Sievert's law region do not show the characteristic change in slope due to local binding.

Pick, Michael A. and Welch, David O. Hydrogen Absorption in the Niobium-Vanadium System. Presented at the International Meeting on Hydrogen in Metals, Münster, Germany, March 6-9, 1979, (to be published in Zeitz, für Phys. Chemil N.F.).

Program: Physical Metallurgy of Metal Hydride Systems

Sponsor: DOE - Office of Basic Energy Sciences,
Materials Sciences Division

PHASE EQUILIBRIA AND HYDROGEN TRAPPING IN DILUTE ALLOYS OF VANADIUM IN NIOBIUM

BNL - 25364

M. A. Pick and D. O. Welch

Metallurgy and Materials Sciences Division

The effect of dilute vanadium additions to niobium on hydrogen absorption was studied by measuring the temperature dependent equilibrium hydrogen partial pressure for pure Nb, Nb+6 at.% V, and Nb+9 at.% V. A theoretical model of the effect of hydrogen trapping on phase equilibria in the α-α' region of such systems was constructed. The results indicate that the H-V binding energy is less than previously thought.[1] A value of .07 eV is obtained from the depression of the α-α' critical temperature, but the shape of the pressure isotherms suggests that this is an upper limit. The measured heat of solution decreases from -37.0 to -38.6 to -38.8 kJg-atom^{-1} going from pure Nb to Nb+6 at.% V to Nb+9 at.% V.

Pick, M. A. and Welch, D. O. Phase Equilibria and Hydrogen Trapping in Dilute Alloys of Vanadium in Niobium. To be presented at the 1979 March Meeting of the American Physical Society, Chicago, IL, March 19-23, 1979. Bull Am. Phys. Soc. <u>24</u>, p. 464 (1979).

Program: Physical Metallurgy of Metal Hydrides Systems

Sponsor: DOE - Office of Basic Energy Sciences,
Materials Sciences Division

THE ENHANCEMENT OF HYDROGEN UPTAKE RATES IN Nb AND Ta BY THIN Pd OVERLAYERS

BNL - 25413

Myron Strongin and M. A. Pick

Metallurgy and Materials Sciences Division

The sticking coefficients, s, for the uptake of hydrogen into the bulk of Nb and Ta[1] are of the order of 0.03 and 0.1, after an uptake of about 15 monolayers. s is found to increase with temperature up to about 500K, where it then decreases rapidly, presumably due to the decreased solubility of H_2. We contend that this temperature dependents on samples cleaned in ultra high vacuum, implies a small barrier for H_2 entry into the bulk. We agrue that the activation is not due to bulk diffusion, since the barrier can be essentially removed by a few monolayers of Pd which implies that the barrier is surface related. With Pd on the surface s for H_2 uptake after the addition of hundreds of layers is about .2 at room temperature, and $P \sim 8 \times 10^{-6}$ Torr, and approaches .4 at about 150°C.

Strongin, Myron and Pick, M. A. The Enhancement of Hydrogen Uptake Rates in Nb and Ta by Thin Pd Overlayers. Presented at American Physical Society, Chicago, IL, March 19-23, 1979.

Program: Physical Metallurgy of Metal Hydride Systems

Sponsor: DOE - Office of Basic Energy Sciences,
Materials Sciences Division

ELECTRON MICROSCOPY OF HYDROGEN DISSOLUTION IN FeTi

BNL - 25423

C. S. Pande and M. A. Pick

Metallurgy and Materials Science Division

FeTi is a candidate material for hydrogen storage systems. We have studied the dissolution of hydrogen in thin film (~1500 Å) FeTi using electron diffraction and transmission electron microscopy. Thin films were prepared by ion milling. The same areas of the foil were observed by T.E.M. before and after hydriding and again after removal of the hydrogen. It was observed that this could be accomplished by further ion milling. Preliminary results indicate that low level of hydrogen dissolution in FeTi results in planar defects (probably due to ordering of hydrogen); and a relatively small increase in dislocation density. Kikuchi lines disappeared on hydriding and were recovered after the removal of hydrogen.

Pande, C. S. and Pick, M. A. Electron Microscopy of Hydrogen Dissolution in FeTi. Presented at Annual TMS-AIME Meeting, New Orleans, LA, Feb. 18-22, 1979.

Programs: Relationship between Properties and Structures (and)
Physical Metallurgy of Metal Hydride Systems

Sponsor: DOE - Office of Basic Energy Sciences,
Materials Sciences Division

THE EFFECT OF CREEP ON FRACTURE OF METALS

BNL - 24506

A. Arbel and J. Warren

Metallurgy and Materials Science Division

Fracture studies were conducted on a commercially pure nickel and solid solution nickel alloy after they crept to various extents. The fracture behavior will be discussed in terms of microstructural changes which took place during the creep process.

Arbel, A. and Warren, J. The Effect of Creep on Fracture of Metals. Presented at the TMS-AIME Fall Meeting, St. Louis, MO, Oct. 15-19, 1978.

Program: Effects of Microstructure and Environment Upon Fracture Toughness

Sponsor: DOE - Office of Basic Energy Sciences,
Materials Sciences Division

THE EFFECT OF CREEP ON SOME RESULTANT MECHANICAL PROPERTIES OF A SOLID SOLUTION NICKEL BASE ALLOY

BNL - 24992

A. Arbel and C. S. Pande

Metallurgy and Materials Science Division

A solid solution nickel base alloy containing a small amount of carbon was annealed so as to minimize its dislocation density and to form stable carbides on its grain boundaries prior to being subjected to creep at various temperatures. The changes in resistance of the alloy to the extension of sharp fatigue precrack in a three point bend charpy type specimens and the changes in tensile properties will be discussed in terms of the microstructure which developed during the creep process.

Arbel, A. and Pande, C. S. The Effect of Creep on Some Resultant Mechanical Properties of a Solid Solution Nickel Base Alloy. Presented at Annual TMS-AIME Meeting, New Orleans, LA, Feb. 18-22, 1979.

Program: Effects of Microstructure and Environment Upon Fracture Toughness

Sponsor: DOE - Office of Basic Energy Sciences,
Materials Sciences Division

DEGRADATION MECHANISMS OF Nb_3Sn COMPOSITE WIRES UNDER TENSILE STRAIN AT 4.2K

BNL - 24266

T. Luhman and M. Suenaga

Metallurgy and Materials Science Division

Nb_3Sn superconducting wires exhibit reversible changes in T_c, J_c, and H_{c2} when strained in tension at 4.2K. Excessive tensile strain eventually causes irreversible degradation of these properties. The mechanisms for this behavior have been studied using a series of monofilament wires with differing bronze to niobium ratios. The onset of irreversible degradation is associated with cracking in the Nb_3Sn compound, observed optically, and with a decreased slope in the I-V curves of the current density measurements. T_c, J_c, and H_{c2} data will be reported for variously heat treated monofilament wires with bronze to niobium ratios from 1:1 to 44:1.

Luhman, T. and Suenaga, M. Degradation Mechanisms of Nb_3Sn Composite Wires Under Tensile Strain at 4.2K. Presented at 1978 Applied Superconductivity Conference, Pittsburgh, PA, Sept. 25-28, 1978. IEEE Trans. on Magnetics, MAG-15, pp. 699-702 (1979).

Program: Superconducting Magnet Conductor Development

Sponsor: DOE - Office of Magnetic Fusion Energy,
Component Development Branch

FABRICATION AND PROPERTIES OF CONDUCTORS FOR FUSION MAGNETS

BNL - 25417

M. Suenaga, T. Luhman, C. Klamut, and W. B. Sampson

Metallurgy and Materials Science Division

The objectives of this project are to develop suitable and economical conductors for fusion magnets, in particular, to develop methods for improving the mechanical properties of Nb_3Sn conductors. This includes the measurement and study of degradation mechanisms of Nb_3Sn conductors under mechanical strain.

Our investigation of degradation in the superconducting properties of Nb_3Sn conductors under mechanical stresses for FY 1977 can be divided into the following areas: 1) monofilamentary Nb_3Sn wires, 2) multifilamentary Nb_3Sn wires and conductors, 3) effects of additives to Nb_3Sn, 4) mechanism for degradation, and 5) construction of high field test facilities. Our effort in FY 1977 has been concentrated in the investigation of T_c, J_c and H_{c2} variations in monofilamentary Nb_3Sn wires. The most important finding in this study is that a Nb_3Sn wire can sustain mechanical strain well beyond "1%" if a proper ratio of the matrix to the Nb core was chosen.

In the area of multifilamentary wires and conductors, a series of seven wire litz conductors was prepared. These conductors will be used to study the mechanical and superconducting properties of Nb_3Sn wires when they are fabricated into a litz conductor. Also, a series of five experimental unreacted Nb_3Sn composite wires was purchased. These five different wires will be used to investigate the effects of variations in Nb to normal metal ratio, Nb filament size and Nb-core composition on the mechanical behavior of Nb_3Sn composite wires. These results will then be compared with those of monofilamentary wires.

In order to gain an understanding of the fracture mechanism of Nb_3Sn layers in the composite, optical and electron microscopic studies of stressed Nb_3Sn wires were initiated. Finally, the description of the high field test facility is given.

Suenaga, M., Kaiho, K., and Luhman, T. Superconducting Properties of Nb_3Sn Wires by Bronze Process. Progress Report FY 1978.

Program: Superconducting Magnet Conductor Development

Sponsor: DOE - Component Development Branch,
Office of Magnetic Fusion Energy

INCREASES IN THE ALLOWABLE STRAIN LIMITS FOR Nb_3Sn WIRE CONDUCTORS BY ALLOYING THE BRONZE MATRIX WITH Be

BNL - 24628

Thomas Luhman

Metallurgy and Materials Science Division

Superconducting critical current densities have been measured as a function of applied tensile strain at 4.2 K and 4.0 tesla on monofilament Nb_3Sn wires containing 0 and 0.03 wt% Be additions to the Cu+11.2 wt% Sn matrices. Typically for a bronze to niobium ratio of 2.5:1 a maximum occurs in the plot of J_c versus strain at 0.6% while the onset of irreversible J_c degradation occurs at a strain value of 1.3-1.4%. Alloying with 0.03 wt% Be increased the strain value for the maximum to 1.0% and increased the strain value marking irreversible J_c degradation to 1.7%. These increases in the allowable strain limits are achieved without decreasing the overall superconducting to normal metal ratio and without any deleterious effects on the superconducting critical current densities at 4.0 tesla.

Luhman, Thomas. Increases in the Allowable Strain Limits for Nb_3Sn Wire Conductors by Alloying the Bronze Matrix with Be. To be published in Journal of Appl. Phys., May 1979.

Program: Superconducting Magnet Conductor Development

Sponsor: DOE - Office of Magnetic Fusion Energy,
Component Development Branch

EFFECTS OF CORE ALLOYING ON THE TENSILE STRAIN - CRITICAL CURRENT DENSITY RELATIONSHIPS IN Nb_3Sn COMPOSITE CONDUCTORS

BNL - 24953

Thomas Luhman, K. Kaiho, and M. Suenaga

Metallurgy and Materials Science Division

Incorporating Ta and Zr alloy additions in the niobium core of Nb_3Sn superconducting wires is known to increase their critical current densities. It is of interest therefore to investigate how these alloy additions effect the dependency of critical current on mechanical tensile strain. Stress-strain and current density-strain measurements were made on monofilament wires having the niobium cores alloyed with 3 to 20 wt%Ta and 1 wt%Zr. Zr alloy additions significantly increase the tensile strains required to permanently degrade the critical current at 4.0 tesla. This effect was a function of the bronze to niobium ratio. No significant differences were found for the Ta alloy additions. The results are interpreted in terms of the present understanding of crack formation in Nb_3Sn layers of the composite conductors.

Luhman, Thomas and Suenaga, M. Increases in the Allowable Strain Limits for Nb_3Sn Wire Conductors by Alloying the Bronze Matrix with Be. Presented at TMS-AIME Fall Meeting, St. Louis, MO, October 15-19, 1978.

Program: Superconducting Magnet Conductor Development

Sponsor: DOE - Office of Magnetic Fusion Energy,
Component Development Branch

SUPERCONDUCTING PROPERTIES OF Nb_3Sn WIRES BY BRONZE PROCESS

BNL - 24983

M. Suenaga, K. Kaiho, and T. Luhman

Metallurgy and Materials Science Division

Improvements in the superconducting critical current density in Nb_3Sn wires are of great interest for their application to magnetic fusion magnets. Recently, alloying Nb cores with Ta in bronze-processed Nb_3Sn wires increased the J_c of these wires at high magnetic field (~10T).[1] We have studied monofilamentary Nb cores, with 7, 10, and 20 wt%Ta and measured $J_c(H)$ up to 18.5T, critical magnetic fields, H_{c2}, and critical temperature, T_c, for wires in which the ratios of the bronze to the core of the wires were 3 and 15. These wires were heat treated for 6 and 15 h at 725°C (longer heat treatments are being made). The H_{c2} of the wires with a ratio of 3 was ~21.5T for all Ta alloyed wires. This value is ~2T higher than a pure Nb_3Sn wire with an equal ratio. However H_{c2} for the wires with a ratio of 15 varied from 16 to 18T as Ta in Nb increased from 7 to 20wt%, while the H_{c2} of the unalloyed Nb_3Sn with the same ratio was ~17T. T_c decreased almost linearly with the alloying content of Ta. T_c of 20wt%Ta core was ~14.5K for the present heat treatment. In addition, we have studied the alloying of the matrix with Ga with the cores as described above. The H_{c2} over the wires of 7, 10, and 20wt%Ta cores with Cu-7.5wt%Sn-5wt%Ga, which were heat treated for 64h at 725°C, was 22.5T for all wires. The results of longer heat treatments for the above wires will also be reported.

Suenaga, M., Kaiho, K., and Luhman, T. Superconducting Properties of Nb_3Sn Wires by Bronze Process. Presented at TMS-AIME Meeting, New Orleans, LA, February 18-22, 1979.

Program: Superconducting Magnet Conductor Development

Sponsor: DOE - Office of Magnetic Fusion Energy,
Component Development Branch

AMORPHOUS SEMICONDUCTORS IN PHOTOVOLTAIC AND SOLAR THERMAL CONVERSION

BNL - 24216

Richard W. Griffith

Metallurgy and Materials Science Division

Amorphous semiconductor materials promise to play an important role in solar energy conversion. For photovoltaic applications, acceptable efficiences η in large-area Schottky cells may be possible if hole transport in a-Si can be improved. Indeed, in very small-area cells ($\sim 1\ \mathrm{mm}^2$) reasonable upper limits $\eta \sim 6\%$ have been reported in the literature. For solar thermal applications, studies on $Si_{1-x}B_x$ alloys point toward the realization of solar coatings that are stable at high temperatures, and that satisfy the dual requirement of high solar absorptance a_s and low infrared emittance e.

Griffith, Richard W. Amorphous Semiconductors in Photovoltaic and Solar Thermal Conversion. Proceedings International Conference Solar Energy Congress, New Delhi, India, January 16-20, 1978, (in press).

Program: Basic Processes and Microstructural Properties of Amorphous Semiconductors

Sponsor: DOE - Office of Basic Energy Sciences, Materials Sciences Division

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PROCESS SCIENCES DIVISION

POLYMER CONCRETE MATERIALS FOR GEOTHERMAL PROCESSES

BNL - 24128

L. E. Kukacka

Process Sciences Division

The feasibility of using polymer concretes as materials of construction in geothermal processes has been established and work to determine the practicability is currently in progress.

High temperature polymer concrete formulations and the technology for using them to produce process components are being developed. Extensive testing at several geothermal sites is in progress. Good durability is indicated.

Studies to identify cost-effective applications are being performed. To date, uses in condensate piping systems, cooling towers, reinjection lines and as a protection for concrete pads have been identified.

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

Program: Alternate Materials of Construction for Geothermal Applications

Sponsor: DOE - Office of Geothermal Energy

POLYMER CONCRETE MATERIALS FOR USE IN GEOTHERMAL ENERGY PROCESSES

BNL - 24214

Lawrence E. Kukacka

Process Sciences Division

The feasibility of using polymer concretes as materials of construction in geothermal processes has been demonstrated and tests to determine the practicability are in progress. High temperature polymer concrete systems have been formulated and laboratory and field tests are being performed in brine, flashing brine, and steam at temperatures up to 500°F (260°C). Results are available from field exposures of up to 18 months in four geothermal environments. Good durability at temperatures > 392°F (200°C) is obtained with samples containing portland cement-silica sand aggregate. Based upon these results, potential applications for polymer concrete in geothermal processes have been identified and the effects of its use on the cost of electric power generation have been estimated. Reductions in the cost of power delivered to the distribution system of ∿ 10% were calculated. Redesign of the plants for the optimum utilization of polymer concrete would be expected to result in greater savings.

Kukacka, L. E. Polymer Concrete Materials for Use in Geothermal Energy Processes. Proc. Second International Congress on Polymers in Concrete, University of Texas at Austin, October 25-27, 1978, pp. 157-72.

Program: Alternate Materials of Construction for Geothermal Applications

Sponsor: DOE - Office of Geothermal Energy

THE STATE-OF-THE-ART OF THE USE OF CONCRETE POLYMER MATERIALS FOR THE REPAIR OF CONCRETE HYDROTECHNICAL STRUCTURES

BNL - 24926

L. E. Kukacka

Process Sciences Division

This report summarizes the current state of the art of the use of concrete polymer materials in the repair of concrete structures and in particular applications in hydrotechnical structures such as spillways, stilling basins, sleuceways, outlets, and canals. Descriptions of the monomer systems and process technology used in the repair processes and the effectiveness of the repairs are given. Results from work performed in the USA and USSR are included.

Program: Alternate Materials of Construction for Geothermal Applications

Sponsor: DOE - Office of Geothermal Energy

THE EFFECT OF DICALCIUM SILICATE (C_2S) AND TRICALCIUM SILICATE (C_3S) ON THE THERMAL STABILITY OF VINYL-TYPE POLYMER CONCRETE

BNL - 24976

T. Sugama and L. E. Kukacka

Process Sciences Division

The effect of anhydrous cement on the thermal stability of vinyl-type polymer concretes has been studied by investigating the chemical interaction between the polymers and the calcium compounds of cement. It was proven from differential scanning calorimetry that C_2S and C_3S have a significant effect on the thermal stability of polymethyl methacrylate and polystyrene. From infrared analysis, the reaction mechanism appears to occur between the calcium oxide in the filler and the $-CH_2-$ groups in the polymer. Polymer concrete containing 17 wt% C_2S maintained excellent strength after exposure for 30 days to 25% brine solutions and to air at 238°C.

Sugama, T. and Kukacka, L. E. The Effect of Dicalcium Silicate (C_2S) and Tricalcium Silicate (C_3S) on the Thermal Stability of Vinyl-Type Polymer Concrete. Cement and Concrete Research 9, (1), pp. 69-76 (1979).

Program: Alternate Materials of Construction for Geothermal Applications

Sponsor: DOE - Office of Geothermal Energy

THE INFLUENCE OF THE CURING AGENT CONCENTRATION AND CURING TEMPERATURES ON THE THERMOSTABILITY OF STYRENE-ACRYLONITRILE-ACRYLAMIDE-TRIMETHYLOLPROPANE TRIMETHACRYLATE COPOLYMER SYSTEMS

BNL 25183

A. N. Zeldin, L. E. Kukacka, J. J. Fontana, N. R. Carciello, and W. Reams

Process Sciences Division

Thermogravimetric (TGA) and Infrared (IR) analyses have been used to determine the thermal stability of a polymer system consisting of styrene-acrylonitrile-acrylamide and trimethylolpropane trimethacrylate. This study indicates that increases in curing temperature and the use of two initiators with different activities decreases the percentages of unreacted monomers. This increases the thermal stability of the polymer. To prove this, dynamic and isothermal TGA were used. The change in typical functional groups found by IR spectra also confirm this observation.

Zeldin, A. N., Kukacka, L. E., Fontana, J. J., Carciello, N. R., and Reams, W. The Influence of the Curing Agent Concentration and Curing Temperatures on the Thermostability of Styrene-Acrylonitrile-Acrylamide-Trimethylolpropane Trimethacrylate Copolymer Systems. J. Appl. Polymer Sci. (submitted).

Program: Alternate Materials of Construction for Geothermal Applications

Sponsor: DOE - Office of Geothermal Energy

ECONOMIC ASSESSMENT OF POLYMER CONCRETE USAGE IN GEOTHERMAL POWER PLANTS

BNL - 50777

Burns and Roe Industrial Services (prepared for L. E. Kukacka)

Process Sciences Division

The objective of this report was to review the Herber and Niland, California 50 MWe conceptual geothermal power plants designs and to identify areas where non-metallic materials, such as polymer concrete, can be technically and economically employed. Emphasis was directed toward determining potential economic advantages and resulting improvements in plant availability. It is estimated that use of polymer concrete in the Heber plant will effect a savings of 6.18 mills per KWH in the cost of power delivered to the network, a savings of 9.7%. A similar savings should be effected in the Niland plant.

Program: Alternate Materials of Construction for Geothermal Applications

Sponsor: DOE - Office of Geothermal Energy

ALTERNATE MATERIALS OF CONSTRUCTION FOR GEOTHERMAL APPLICATIONS, PROGRESS REPORT NO. 15, OCTOBER 1977-MARCH 1978

BNL - 50834

L. E. Kukacka, J. Fontana, A. Zeldin, T. Sugama, W. Horn, N. Carciello, J. Amaro, and W. Reams

Process Sciences Division

A program to determine if non-metallic materials such as polymers, concrete polymer composites, and refractory cements can be utilized as materials of construction in geothermal processes is in progress. To date, several high temperature polymer concrete systems have been formulated, laboratory and field tests performed in brine, flashing brine, and steam at temperatures up to 260°C (500°F), and economic studies started. Laboratory data for exposure times > 2 years are available. Results are also available from field exposures of up to 24 months in four geothermal environments. Good durability is indicated. Work at four of these sites is continuing and plans to initiate tests at other sites are being implemented. Work accomplished during the period October 1977-March 1978 is described in the current report.

BNL Progress Report, October 1977-March 1978.

Program: Alternate Materials of Construction for Geothermal Applications

Sponsor: DOE - Office of Geothermal Energy

ALTERNATE MATERIALS OF CONSTRUCTION FOR GEOTHERMAL APPLICATIONS, PROGRESS REPORT NO. 16, APRIL-SEPTEMBER 1978

BNL - 50925

L. E. Kukacka, J. Fontana, A. Zeldin, J. Amaro, T. Sugama, N. Carciello, and W. Reams

Process Sciences Division

A program to determine if non-metallic materials such as polymers, concrete polymer composites, and refractory cements can be utilized as materials of construction in geothermal processes is in progress. To date, several high temperature polymer concrete systems have been formulated, laboratory, and field tests performed in brine, flashing brine, and steam at temperatures up to 260°C (500°F), and economic studies started. Laboratory data for exposure times > 2 years are available. Results are also available from field exposures of up to 24 months in five geothermal environments. Good durability is indicated. Work at four of these sites is continuing and plans to initiate tests at other sites are being implemented. Work accomplished during the period April-September 1978 is described in the current report.

BNL Progress Report, April-September 1978.

Program: Alternate Materials of Construction for Geothermal Applications

Sponsor: DOE - Office of Geothermal Energy

CONCRETE POLYMER MATERIALS FOR GEOTHERMAL APPLICATIONS

BNL - 24215

Arkady Zeldin, Lawrence E. Kukacka and Neal Carciello

Process Sciences Division

The feasibility of using a copolymer composed of styrene, acrylonitrile, and acrylamide or methacrylamide in the formation of a high strength thermally and chemically stable polymer concrete for use in geothermal environments has been demonstrated. Specimens produced with the copolymer in conjunction with an aggregate containing sand and portland cement had compressive strengths in the range 25,000 to 30,000 psi and were thermally stable up to ∿ $240^{\circ}C$.

A study of the effect of monomer concentration on the properties of the polymer concrete indicated that the optimum concentration is in the range 12 to 13 wt%. Increased monomer concentration lead to a nonuniform polymer distribution within the composite, resulting in a deterioration of the properties. The optimum properties are obtained when the monomer is used in conjunction with an aggregate containing 70 to 80 wt% silica sand and 20 to 30 wt% portland cement.

The results from laboratory and field evaluations in progress indicate that the materials can be used for pipe or as protective liners on pipe and vessels in electric generating and direct utilization geothermal processes.

Zeldin, A., Kukacka, L. E., and Carciello, N. Concrete Polymer Materials for Geothermal Applications. Presented at AIChE Symposium, Philadelphia, Pennsylvania, June 4-8, 1978.

Program: Cementing of Geothermal Wells

Sponsor: DOE - Office of Geothermal Energy

CEMENTING OF GEOTHERMAL WELLS, PROGRESS REPORT NO. 7, OCTOBER-DECEMBER 1977

BNL - 50808

L. E. Kukacka, J. Fontana, A. Zeldin, N. Carciello, T. Sugama, G. L. Kalousek,
T. J. Rockett, B. E. Simpson, R. S. Kalyoncu, D. M. Roy, and D. K. Curtice

Process Sciences Division

A coordinated program for the development of improved cements specifically designed for geothermal well applications was started in April 1976. Since that time an assessment of the state of the art of well cementing has been made, a management plan prepared, and research on organic and inorganic cementing materials started. Work accomplished during the period October 1-December 31, 1977 is described in the current report.

BNL Progress Report, October-December 1977

Program: Cementing of Geothermal Wells

Sponsor: DOE - Office of Geothermal Energy

CEMENTING OF GEOTHERMAL WELLS, PROGRESS REPORT NO. 8, JANUARY-MARCH 1978

BNL - 50850

L. E. Kukacka, J. Fontana, T. Sugama, T. J. Rockett, R. S. Kalyoncu, D. K. Curtice, E. R. Fuller, A. Zeldin, N. Carciello, W. Reams, G. L. Kalousek, B. E. Simpson, and D. M. Roy

Process Sciences Division

A coordinated program for the development of improved cements specifically designed for geothermal well applications was started in April 1976. Since that time an assessment of the state of the art of well cementing has been made, a management plan prepared, and research on organic and inorganic cementing materials started. Work accomplished during the period January 1-March 31, 1978 is described in the current report.

BNL Progress Report, January-March 1978

Program: Cementing of Geothermal Wells

Sponsor: DOE - Office of Geothermal Energy

CEMENTING OF GEOTHERMAL WELLS, PROGRESS REPORT NO. 9, APRIL - JUNE 1978.

BNL - 50911

L. E. Kukacka, J. Fontana, T. Sugama, T. J. Rockett, R. S. Kalyoncu, A. Zeldin,
D. K. Curtice, N. Carciello, G. L. Kalousek, B. E. Simpson, and D. M. Roy

Process Sciences Division

Work to implement the program plan for the development of improved high temperature cementing materials for geothermal wells is continuing. Research work is currently in progress at Brookhaven National Laboratory, Battelle's Columbus Laboratories, Colorado School of Mines, Dowell, Pennsylvania State University, Southwest Research Institute, University of Rhode Island and the National Bureau of Standards.

Work on the first element of the program management plan (problem definition) has been completed by Dowell and a report issued. The materials development and property verification phases of the plan are in progress.

The first meeting of the "Geothermal Well Cement Advisory Panel" since it became affiliated as a Task Group of the American Petroleum Institute was held on June 20-21, 1978. All segments of the well completion industry were present at the meeting. The agenda for the meeting included technical presentations by the participants in the materials development and property verification phases of the program, a general discussion of the work and problems associated with the use of the technology by industry, and a visit to an oil well site.

Work on PC containing mixtures of organosiloxanes and styrene is continuing to show the potential of the system as a high temperature cementing material. Samples exposed for 360 hr to brine at 250°C have not shown evidence of hydrolysis and have maintained high strength. At 350°C, the compressive strength is > 5000 psi. Preliminary tests to determine the pumpability of the system are in progress.

Work on the development of inorganic cementing materials is continuing at six laboratories. Several promising materials have been identified. Tests to measure compressive strengths, bond strengths, permeability, and compatibility with drilling muds are in progress. Consistometer tests have been performed on some materials.

Based upon preliminary results from the program, workers at the Los Alamos Scientific Laboratory have requested assistance in the selection of a material for use in the remedial cementing of hot dry rock well. As a precursor to the selection of a material, property verification tests on several candidate materials will be started at the National Bureau of Standards in August. Cements to be tested include a hydrothermal cement, two polymer cements and a Type G modified with silica flour. A recommendation for a material will be made in late October. The remedial cementing is scheduled for late 1978. If implemented, this will represent the first down-hole test of a cement developed in the program.

BNL Progress Report, April-June 1978.

Program: Cementing of Geothermal Wells

Sponsor: DOE - Office of Geothermal Energy

CEMENTING OF GEOTHERMAL WELLS, PROGRESS REPORT NO. 10, JULY - SEPTEMBER 1978

BNL - 50943

L.E. Kukacka, J. Fontana, T. Sugama, T.J. Rockett, R.S. Kalyoncu, D.K. Curtice, E.R. Fuller, A. Zeldin, N. Carciello, W. Reams, B.E. Simpson, D.M. Roy

Process Sciences Division

Work to implement the program plan for the development of improved high temperature cementing materials for geothermal wells is continuing. Research work is currently in progress at Brookhaven National Laboratory, Battelle's Columbus Laboratories, Dowell, Pennsylvania State University, Southwest Research Institute, University of Rhode Island and the National Bureau of Standards. Experimental work has been completed at the Colorado School of Mines and a final report is being prepared. Samples of β-dicalcium silicate-silica cement developed in this program have been submitted for additional evaluation at Dowell and the National Bureau of Standards.

Phase II of Dowell's program is continuing. The initial screening portion of this work has identified several promising systems that will undergo more rigorous testing. Dynamic brine exposure testing of several systems has been initiated at the East Mesa Geothermal Test Facility. Testing at the Niland test site is scheduled to start soon.

Property verification tests on cements produced in the materials development phase of the program were initiated at the Bureau of Standards. Preliminary data are available for five cements exposed for 176 hr to water at a temperature of 195°C. Three of the cements exhibited strength losses during the test. An aluminum hydroxide cement and a polymer cement showed slight increases in strength after the exposure. These and longer-term data will be utilized in the selection of a material for use in the remedial cementing of a hot dry rock well at the Los Alamos Scientific Laboratory. A recommendation for a material will be made in December. The remedial cementing is scheduled for January 1979. If implemented, this will represent the first down-hole test of a cement developed in the program.

BNL Progress Report, July-September 1978.

Program: Cementing of Geothermal Wells

Sponsor: DOE - Office of Geothermal Energy

THIN SAND FILLED RESIN OVERLAYS

BNL - 24079

Jack J. Fontana and Ronald Webster

Process Sciences Division

The use of thin sand filled resinous overlays to prevent the penetration of water and deicing salts into portland cement concrete (PCC) bridge and overpass decks has been investigated. Sealing of PCC surfaces and the provision of a new durable skid resistant surface cannot be attained with conventional PCC or asphalt materials. An overaly composed of multiple layers of synthetic thermosetting resins and clean, dry, ground grain silica sand which reduces the penetration of water by over 94% has been developed.

It has been shown by others that membranes are considered impermeable to water if the electrical resistance across the membrane is greater than 5×10^5 ohms/sq ft after saturation with water for 24 hours. All the aggregate filled resinous overlay systems tested have electrical resistances greater than 19×10^6 ohms/sq ft after 24 hours. Several systems have shown electrical resistances greater than 19×10^6 ohms/sq ft after 28 days of water saturation.

The bonding of the overlay to PCC, as measured by the shear strength at the interface, is greater than the shear strength of PCC in most cases.

Field applications have been made by highway maintenance crews with available highway equipment. The New York State Department of Transportation (NYS DOT) has measured the skid resistance of the overlay surface with their skid trailer and found it to have a SN of 46. The materials cost of such an overlay is approximately $7.50/sq yd.

Fontana, J. J. and Webster, R. Thin Sand Filled Resin Overlays. Presented at 2nd International Congress on Polymers in Concrete, Austin, Texas, October 25-27, 1978.

Program: Implementation of Concrete Polymer Research on Repair of Deteriorated Concrete

Sponsor: FHWA - Implementation Division

THIN POLYMER CONCRETE OVERLAYS - INTERIM USERS' MANUAL

BNL - 24110

R. Webster, J. Fontana, and L. E. Kukacka

Process Sciences Division

This interim users' manual outlines the procedures for the use and placement of thin polymer-concrete overlays on concrete bridge decks.

The overlay, which consists of alternating layers of monomer and aggregate, is highly impermeable to the penetration of chlorides and water. Each layer of the overlay cures rapidly, in one to three hours. Excellent bond strength, in excess of 500 psi (3.45 MPa), can be developed between the overlay and dry and clean, sound concrete. In addition, the overlay shows potential as a means of restoring the skid resistance of polished pavement.

Program: Implementation of Concrete Polymer Research on Repair of Deteriorated Concrete

Sponsor: FHWA - Implementation Division

RAPID PATCHING OF DETERIORATED CONCRETE USING POLYMER CONCRETE

BNL 24217

Jack J. Fontana, Ronald Webster, and L. E. Kukacka

Process Sciences Division

The increased use of deicing salts is resulting in rapid deterioration of portland cement concrete bridge decks. Corrosion of the reinforcing steel by the chlorides results in an increase in the volume of the steel. This expansion produces stresses in the concrete which result in delaminations and surface spalling. The repair of spalls with conventional durable patching materials can only be made if traffic can be diverted from the patched areas for several days. Therefore, a durable patching material which will allow traffic to be resumed over the repaired area in a few hours is needed. These criteria can be met by the use of polymer concrete.

Polymer concrete (PC) is a composite material in which the aggregate is bound togehter in a dense matrix with a polymeric binder. The aggregate is mixed with a monomer mixture and subsequently cured in place. PC combines the premix characteristics of portland cement concrete with high strength, long-term durability, and short cure time. The high early strength of PC is suitable for use in the repair of highway structures where traffic conditions allow closing of the area for only a few hours.

Fontana, J. J., Webster, R., and Kukacka, L. E. Rapid Patching of Deteriorated Concrete Using Polymer Concrete. Presented at 2nd International Congress on Polymers in Concrete, Austin, Texas, October 25-27, 1978.

Program: Implementation of Concrete Polymer Research on Repair of Deteriorated Concrete

Sponsor: FHWA - Implementation Division

RAPID PATCHING OF CONCRETE USING POLYMER CONCRETE

BNL - 25236

Ronald P. Webster, Jack J. Fontana, and L. E. Kukacka

Process Sciences Division

One of the major problems confronting the highway industry today is the need for a rapid repair material for deteriorated concrete structures. High maintenance costs and traffic delays have created the need for a long lasting, rapid setting, concrete patching material.

The use of polymer concrete (PC) as a repair material is discussed. Materials used to make polymer concrete composites are described, as is the procedure for placing polymer concrete patches. The placement of polymer concrete patches in the field by highway maintenance personnel using conventional concrete mixing equipment and techniques is also described

Webster, R. P., Fontana, J., and Kukacka, L. E. Rapid Patching of Concrete Using Polymer Concrete. Presented at Continuously Reinforced Pavement Workshop, New Orleans, Louisiana, February 15-16, 1978.

Program: Implementation of Concrete Polymer Research on Repair of Deteriorated Concrete

Sponsor: FHWA - Implementation Division

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

BNL - 25396

Ronald P. Webster and Jack J. Fontana

Process Sciences Division

The highway construction industry uses several billion tons of aggregate annually in the construction of highway pavement and bridge decks. In the interest of highway safety and maintenance, it is important that the aggregates used for pavement surfacing systems possess a high resistance to polishing as well as a high resistance to wear and weathering. Unfortunately, the supply of natural aggregates satisfying these criteria is being rapidly depleted in many areas of the United States, necessitating the shipment of large quantities of high quality aggregate to these regions.

Presented is a discussion of the preliminary phase of a research program being conducted to investigate impregnation materials and techniques to improve the wear resistance properties of natural aggregates, thereby making them acceptable for use in pavement surfacing systems. Test results obtained during this phase of the research program are discussed.

Webster, R. P. and Fontana, J. J. Improvement of Wear-Resistance Properties of Natural Aggregates by Materials Impregnation. Presented at the 1978 FCP Research Review Conference, College Park, Maryland, October 3-6, 1978.

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

Sponsor: FHWA - Implementation Division

DEVELOPMENT OF A GLASS POLYMER COMPOSITE SEWER PIPE FROM WASTE GLASS, PROGRESS REPORT NO. 6, OCTOBER-DECEMBER 1977

BNL - 50790

L. E. Kukacka, J. Fontana, R. Rayfiel, G. Arnold, and B. Galen

Process Sciences Division

Large quantities of energy can be conserved by recycling municipal solid waste. Reductions in the costs associated with waste disposal such as by landfilling can also be accrued. While uses for recycled ferrous and non-ferrous metals are apparent, uses for the glass fraction which constitutes ∿ 10% of municipal solid waste, have not been developed. As a result, a program to develop methods for incorporating waste glass into composites which can be used for construction materials was started in July 1976. Since that time the properties of as-produced glass polymer composite (GPC) sewer pipe have been measured, durability tests started, field testing of full-scale specimens initiated, and calculations made to determine the energy requirements and costs. Work accomplished during the period October 1-December 31, 1977 is described in the current report.

BNL Progress Report, October-December 1977.

Program: Development of a Glass-Polymer Composite Sewer Pipe from Waste Glass

Sponsor: DOE - Office of Industrial Energy Conservation

DEVELOPMENT OF A GLASS POLYMER COMPOSITE SEWER PIPE FROM WASTE GLASS, PROGRESS REPORT NO. 7, JANUARY-MARCH 1978

BNL - 50835

L. E. Kukacka, J. Fontana, R. Rayfiel, G. Arnold, and B. Galen

Process Sciences Division

Large quantities of energy can be conserved by recycling municipal solid waste. Reductions in the costs associated with waste disposal such as by landfilling can also be accrued. While uses for recycled ferrous and non-ferrous metals are apparent, uses for the glass fraction which constitutes ∿ 10% of municipal solid waste, have not been developed. As a result, a program to develop methods for incorporating waste glass into composites which can be used for construction materials was started in July 1976. Since that time the properties of as-produced glass polymer composite (GPC) sewer pipe have been measured, durability tests started and field testing of full-scale specimens initiated. Based upon the as-produced properties, calculations have been made to determine the energy requirements and costs. Work accomplished during the period January 1-March 31, 1978 is described in the current report.

BNL Progress Report, January-March 1978.

Program: Development of a Glass-Polymer Composite Sewer Pipe from Waste Glass

Sponsor: DOE - Office of Industrial Energy Conservation

DEVELOPMENT OF A GLASS POLYMER COMPOSITE SEWER PIPE FROM WASTE GLASS, PROGRESS REPORT NO. 8, APRIL-JUNE 1978

BNL - 50886

L. E. Kukacka, J. Fontana, R. Rayfiel, G. Arnold, and B. Galen

Process Sciences Division

Large quantities of energy can be conserved by recycling municipal solid waste. Reductions in the costs associated with waste disposal such as by landfilling can also be accrued. While uses for recycled ferrous and non-ferrous metals are apparent, uses for the glass fraction which constitutes ∿ 10% of municipal solid waste, have not been developed. As a result, a program to develop methods for incorporating waste glass into composites which can be used for construction materials was started in July 1976. Since that time the properties of as-produced glass polymer composite (GPC) sewer pipe have been measured, durability tests in hot water and sulfuric acid started, and field testing of full-scale specimens initiated. Work to optimize the mix formulation is in progress. Based upon the as-produced properties, calculations have been made to determine the energy requirements and costs. Conservation and economic benefits are indicated. Work accomplished during the period April 1-June 30, 1978 is described in the current report.

BNL Progress Report, April-June 1978

Program: Development of a Glass-Polymer Composite Sewer Pipe from Waste Glass

Sponsor: DOE - Office of Industrial Energy Conservation

REACTION, PROCESS, AND COST ENGINEERING FOR THE FLASH HYDROPYROLYSIS (FHP) OF COAL

BNL - 25232

Meyer Steinberg, Peter Fallon, Vi-Duong Dang, B. Bhatt, E. Zeigler, and Quinton Lee

Process Sciences Division

The latest experimental data on the Flash Hydropyrolysis of North Dakota lignite in the 2 lb/hr entrained tubular reactor experimental facility are summarized. The range of conditions investigated covers reactor pressures from 500 psi to 4000 psi, temperatures from 500° to 900°C, and coal particle residence times in the reactor from 1 to 10 seconds. The major effects of the process variables on the yields of liquid hydrocarbons consisting mainly of BTX and heavy oils ($\geq C_9$) and hydrocarbon gases consisting mainly of methane and ethane and small amounts of carbon oxides are summarized. The product for maximum carbon conversion to liquid was obtained at 725°C and 2000 psi and amounts to 10% BTX, 10% oils, 25% methane, 10% ethane, and 6% CO. A maximum gaseous yield was obtained at 875°C and 2500 psi and amounts to 88% methane, 0.5 ethane, 1.3% CO and < 1% BTX. The optimum coal residence time in the tubular reactor for the liquid condition is ∿ 7 seconds and for gases it is ∿ 2 seconds. Possibilities exist for improving gas effluent compositions under dense phase operation. A three-step reaction model is developed in an attempt to obtain generalized expressions of the hydrocarbon component yields as a function of pressure, temperature and residence time. The experimental data have been fitted to Arrhenius type rate equations taking into account formation and decomposition of major products. Activation energies indicate mainly a chemical reaction controlled mechanism. The use of these rate equations in conjunction with heat balance expressions are described for the design of a hydropyrolysis reaction vessel. Additional experimental, design, and analysis work is needed to obtain a much more detailed understanding of the reactor engineering. Process design and preliminary economic estimates are made for three versions of the FHP process system: (1) producing only liquid products for motor gasoline fuel, (2) producing both liquid and gaseous hydrocarbon products for motor gasoline and pipeline gas, and (3) producing only gaseous products for pipeline gas. For comparable overall values of coal conversions (62%), the minimum cost is obtained for the combined production of motor gasoline and pipeline gas. The largest factor (∿ 35%) in the capital cost of the FHP plant is the equipment needed for recycling and conditioning and hydrogen process gas. The FHP process has the advantage of allowing effective gas-solid and gas-liquid separation operations for producing hydrocarbon products from the unconverted

char, oils, and process gas. The FHP system also has the distinct advantage of versatility and process flexibility for varying the product slate and the production rate of gaseous and liquid hydrocarbon fuel products in the same reactor depending on reactor operating conditions.

Steinberg, M., Fallon, P., Dang, V., Ziegler, E. and Lee, Q. Reaction, Process and Cost Engineering for the Flash Hydropyrolysis (FHP) of Coal. Presented at 71st Annual Meeting of American Institute of Chemical Engineers, Miami, Florida, November 12-16, 1978.

Program: Flash Hydropyrolysis of Coal

Sponsor: DOE - Office of Fossil Fuel Processing, Gasification Development

FLASH HYDROPYROLYSIS OF COAL, PROGRESS REPORT NO. 3, JULY 1-SEPTEMBER 30, 1977

BNL - 50779

Meyer Steinberg and Peter Fallon

Process Sciences Division

The program is designed to study the process variables and chemistry of the Flash Hydropyrolysis Process, a rapid gas-phase, non-catalytic coal hydrogenation technique developed at BNL. The equipment used is a 1 lb/hr unit utilizing a 1 inch down-flow tubular reactor designed to operate at up to 4000 psi and 800°C. This equipment has been in operation for more than a year with only one major problem, the rupture of the hydrogen preheater. Metallurgical examination of the affected area determined the rupture to have been caused by hydrogen embrittlement of the Inconel 601 alloy used in the fabrication of the preheater. A replacement preheater made of Inconel 617 has been operating sucessfully for more than 100 hours during the past year.

Coal and char analysis continue to be done on a routine basis. A boiling range determination was made on a sample of the liquid product. Approximately 50% of the liquid was distilled up to temperatures of 210°C before the condenser filled with solids. An analysis of the condenser and flask residues showed them to contain small quantities of both sulfur and nitrogen. A sulfur analyzer has been ordered to allow more rapid and frequent analysis of the liquids and solids.

All the data to date on product yield as a function of temperature and hydrogen pressure is correlated in four tables and plotted in a series of nine figures. The total liquid yields appear to reach a maximum of approximately 20% at 750°C with only slight increases with hydrogen pressures above 2000 psi. Approximately half of this yield is BTX (benzene, toluene, xylene). The ethane yield also appears to maximize between 700 and 750°C but continues to increase with increased pressure. Methane yields are shown to continue to increase with both temperature and hydrogen pressure. Total carbon conversion under these conditions approximated 60%.

The pyrolysis of lignite using helium in the system shows a five to ten fold decrease in the yields of CH_4, C_2H_6, and C_6H_6 compared to flash hydropyrolysis under hydrogen pressure.

Preliminary experiments were conducted at 750° and 800°C to determine the effect of coal particle residence time on product yields and distribution.

The results indicate that a 750°C both liquid and gaseous yields increase from 45 to 52% as the residence time is increased by a factor of four from 2.3 to 9.2 seconds. However, at 800°C under similar conditions, little change in total yield decreases from approximately 4 to 1% with a corresponding increase in gaseous products.

BNL Progress Report, July 1-September 30, 1977.

Program: Flash Hydropyrolysis of Coal

Sponsor: DOE - Office of Fossil Energy

FLASH HYDROPYROLYSIS OF COAL, PROGRESS REPORT NO. 4, OCTOBER 1-DECEMBER 31, 1977

BNL - 50821

Meyer Steinberg and Peter Fallon

Process Sciences Division

The principal objective of this program is to experimentally study the process variables and chemistry of the Flash Hydropyrolysis Process, a rapid gas-phase, non-catalytic coal hydrogenation technique developed at BNL for the conversion to gaseous and liquid fuels. The experimental equipment used for this purpose is a highly instrumented 1-in. down-flow tubular reactor originally designed to operate at up to 4000 psi and 800°C, with coal feed up to 1 lb/hr. These conditions are being extended to include temperatures to 900°C at pressures $\geq$ 2500 psi and coal feed to 2 lbs/hr. The equipment has been operated for more than a year with only one major problem, the failure of the original electric resistance hydrogen preheater. This has been replaced with one fabricated from a superior alloy.

Coal and char analysis are continuing to be performed on a routine basis. The water produced in the hydrogenation reaction and collected with the liquid hydrocarbon product is being studied for such components as phenols and ammonia in order to further close the material balances. The possibility of phenols in the aqueous phase has become of particular interest since in two analyses performed by other laboratories on the collected liquid hydrocarbons produced, phenols were reported by one and not the other.

A second distillation curve was performed on the total organic liquid product, this time extending the distillation temperature range to 350°C. The results were similar to the first curve indicating that the liquid contains approximately 50% BTX (benzene, toluene, xylene) and 50% heavier hydrocarbons. A sulfur analyzer has been received, assembled and tested and found to be reproducible to within ± 1.2% for analysis of sulfur in coal, coke and char.

Attempts to operate the experimental equipment at its maximum design pressure, 4000 psi, during this quarter has had limited success. Most of the problems were associated with leaks in the process gas sampling taps, requiring some modifications to this system.

A major portion of the experimental effort was devoted to the study of the effect of coal particle residence time. In some cases, the total hydrocarbon yields were observed to decrease with increased residence time and in most cases, the carbon monoxide increased with increasing residence time. The reduction in hydrocarbon yield occurred in different runs conducted at low pressure (500 psi) and in runs conducted at temperatures of $\geq$ 800°C. At 500 psi as much as a 40% reduction in methane was observed as the residence time increased from approximately 1 to 4.5 seconds. A loss in hydrocarbon yield could only be caused by the products either coking or forming a product such as the heavier liquid hydrocarbons ($\geq C_9$) which are not measured by the on-line chromatograph.

A number of exploratory runs were also conducted including the use of a Battelle Treated Coal (BTC-caking coal treated with CaO), a New Mexico sub-bituminous coal, a mixture of lignite and lignite char and a lignite impregnated with iron. The BTC ran well in the reactor with no caking and gives a total hydrocarbon yield of 51% with 20% liquids based on conversion of the carbon feed. Although the sub-bituminous coal produced a total hydrocarbon yield of only 41.8% with 13.7% liquids, the experimental conditions used were those found to give substantial yields for lignite and may not be ideal for sub-bituminous. The lignite-char mixture gave improved results, 12.2% BTX and a total hydrocarbon yield of 64.6%. These results were calculated on the carbon in the fresh coal feed and some of the yields could have originated from unreacted portions of the char. The result of significance for the experiment using iron was a 61% increase in BTX yield (from 7.6% to 12.2% carbon conversion), an 80% increase in ethane yield (from 5.5% to 9.9%) and a 49% decrease in light oils. These results need repetition for confirmation.

BNL Progress Report, October 1-December 31, 1977.

Program: Flash Hydropyrolysis of Coal

Sponsor: DOE - Office of Fossil Energy

FLASH HYDROPYROLYSIS OF COAL, PROGRESS REPORT NO. 5, JANUARY-MARCH 31, 1978

BNL - 50894

Meyer Steinberg and Peter Fallon

Process Sciences Divison

The experimental equipment and on-line process gas chromatograph continue to operate with increased reliability and satisfaction. It is anticipated that the present experimental program of approximately three runs per week will be expanded to approximately four runs per week. The determination and identification of the heavier liquid hydrocarbons ($\geq C_9$) is progressing although a satisfactory on-line method of measurement has yet to be developed. A number of liquid samples from experiments using lignite and sub-bituminous coal plus one using a treated bituminous coal have been examined. Generally, it is found that those liquids produced at the higher reactor temperatures contain considerably more BTX than heavier hydrocarbon ($\geq C_9$) although the overall yield of liquids tends to decrease rapidly at these higher temperatures (> 775°C).

Nitrogen balances are now being made on selected runs. The results show as much as 50% remains in the char, 25 to 30% appears in the gas and the remainder is contained in the water produced as ammonia. Sulfur balances continue to be a problem partly due to the inadequate performance of an instrument purchased for this purpose.

Experiments conducted at 2000 psi and 2500 psi hydrogen pressure using lignite, with and without preheating the hydrogen to reactor temperature and at reactor temperatures between 725° and 900°C, show a very significant effect of product and coal particle residence time on both product yield and distribution. Even at a temperature as low as 750°C, some decomposition of the BTX product was observed as the residence time in the reactor exceeded approximately 7 seconds. As the reactor temperature increased, the degree and rate of BTX decomposition increased. The maximum BTX yield was approximately the same ($\approx$ 9%) whether the hydrogen was preheated or not. The ethane yields, for the same series of experiments were slightly greater than the BTX yields and followed the same trend except they were more stable with less decomposition.

Significant decomposition of the methane was not observed until reactor temperatures of 850° to 875°C were reached. At 875°C and above when the hydrogen was not preheated, as much as 4 to 6% of the methane was lost by decomposition as the residence time was increased from approximately 5 seconds to 10 seconds.

A few similar experiments using a sub-bituminious coal and preheated hydrogen were also conducted. The results follow closely those of the lignite except for a large increase ($\approx$ 20%) in the ethane yields.

Some of the experimental data was fitted to two mathematical expressions, one empirical and the other developed from the kinetics of the system and the process variables. The empirical expression was developed from the total conversion recorded for the first 62 experimental runs, and aside from approximately 6 points, the fit appears to be as good as the second expression. This expression was obtained from 32 data points taken from 8 experimental runs conducted at 2500 psi and between the temperatures of 725° and 900°C. The correlation coefficient was 0.92 indicating excellent agreement with the experimental data.

BNL Progress Report, January-March 31, 1978.

Program: Flash Hydropyrolysis of Coal

Sponsor: DOE - Office of Fossil Energy

FLASH HYDROPYROLYSIS OF COAL, PROGRESS REPORT NO. 6, APR. 1-JUNE 30, 1978

BNL - 50948

Meyer Steinberg and Peter Fallon

Process Sciences Division

During this report period, thirty experimental runs were conducted between pressures of 500 and 2500 psig and temperatures of 850° and 900°C for the purpose of studying the production of gaseous hydrocarbons from lignite. Yields as high as 90% conversion of the available carbon to methane and ethane have been observed at 2500 psig and 875°C, with only 1.5% of the carbon appearing as CO and the remainder as char. It was observed that significant decomposition of the gaseous hydrocarbon products occurred as the coal residence time in the reactor increased from the maximum yields at 2.4 sec to 7 seconds.

Hydrogen pressure was shown to have a significant effect on the production of the gaseous hydrocarbons at 875-900°C, the yield increasing linearly at a rate of 18% in absolute conversion of the available carbon for each 500 psi increase in pressure.

Direct measurement of coal particle residence times are now possible. Initial comparison of the first five runs in which accurate measurements were made shows the calculated value to be within 26% of the measured value and in some cases to be in very good agreement.

A comparison was made of the coal hydrogenation data from IGT (The Institute of Gas Technology), CSRD (Cities Service Research and Development Company), PERC (The Pittsburgh Energy Research Center, and BNL. Both the IGT and CSRD data were from coal liquefaction studies while PERC data concentrates on coal gasification. In comparing the liquefaction data, the BNL results appears to give slightly better liquid yields under similar conditions than either IGT or CSRD. At the same conditions, the BNL data also show slightly greater gaseous yields than IGT and about the same gaseous yields as CSRD.

Since the conditions of hydrogen to coal feed ratio was considerably different for the BNL and PERC data, a direct comparison was not possible. By correlating the data from both groups, it was shown the gaseous hydrocarbon yield to be a function of the hydrogen to coal feed ratio to the one-fifth power. It was also shown that at even the lowest ratio (most concentrated gas stream) the methane concentration is not more than 75% of the equilibrium value (for the reaction $C+2H_2=CH_4$) and therefore, the reaction is not being equilibrium limited.

In order to operate the experimental equipment in a region of temperature and pressure needed to study the formation of gaseous hydrocarbons mainly, the experimental limits of the reactor were changed from 4000 psig and 800°C to 2500 psig and 900°C. Both these limits are within the 10,000 hour life expectancy of the Inconel 617 material of the reactor tube.

BNL Progress Report, April 1-June 30, 1978.

Program: Flash Hydropyrolysis of Coal

Sponsor: DOE - Office of Fossil Energy

FLUIDIZED-BED COMBUSTION OF COAL WITH LIME ADDITIVES. KINETICS AND MECHANISM OF REGENERATION OF THE LIME SORBENT

BNL - 24438

James M. Chen and Ralph T. Yang

Process Sciences Division

The apparent solid-solid reaction between CaS and $CaSO_4$ is the rate-controlling reaction in the lime sorbent regeneration for fluidized-bed combustion of coal, as well as in some other important industrial processes such as the sulfuric acid-cement process. A two-step mechanism for this reaction involving SO_3 was determined. The rate-controlling step in the mechanism is the decomposition of $CaSO_4$ to form CaO and SO_3. Kinetics and rate expressions are established for the overall reaction and the separate steps. Results are also presented for the kinetics and the thermodynamics of all the possible reactions under the conditions of the aforementioned processes.

Chen, J. M. and Yang, R. T. Fluidized-Bed Combustion of Coal with Lime Additives. Kinetics and Mechanism of Regeneration of the Lime Sorbent. Ind. Eng. Chem. Fundamentals (in press).

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

Sponsor: DOE - Office of Fossil Energy

DIRECT EVIDENCE FOR THE EXISTENCE OF GASEOUS INTERMEDIATES IN THE CaS-CaSO$_4$ REACTION

BNL - 24439R

Ralph T. Yang and Ming-Shing Shen

Process Sciences Division

By reacting physically separated CaS and CaSO$_4$ discs, direct evidence was provided for the existence of gaseous intermediates in the CaS-CaSO$_4$ reaction. Reaction product analyses further showed that the gaseous intermediates are likely supplied by the CaSO$_4$ decomposition.

Shen, M. and Yang, R. T. Direct Evidence for the Existence of Gaseous Intermediates in the CaS-CaSO$_4$ Reaction. AIChE Journal R&D Notes (in press).

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

Sponsor: DOE - Office of Fossil Energy

CATALYTIC FLUIDIZED-BED COMBUSTION OF COAL. ENHANCEMENT OF SULFATION AND REGENERATION OF CALCIUM OXIDE BY IRON OXIDE

BNL - 24653

Ralph T. Yang and Ming-Shing Shen

Process Sciences Division

A small amount of iron oxide coated on the surface of limestone substantially increases both the rate and the ultimate capacity for SO_2 sorption. The iron oxide also catalyzes the reductive regeneration reaction of the sorbent from the sulfated calcium oxide. Evidence is presented which shows that such catalytic effects are chemical in nature, rather than due to pore enlargement. Fluidization tests at 900°C showed that no added attrition of the sorbent particles was caused by the coated iron oxide. Practical aspects of application of the catalytic effects to fluidized-bed combustion of coal to improve the sulfur retention efficiency and lime requirement for both once-through and regenerative systems are discussed.

Yang, R. T. and Shen, M. Catalytic Fluidized-bed Combustion of Coal. Enhancement of Sulfation and Regeneration of Calcium Oxide by Iron Oxide. Ind. Eng. Chem. Proc. Des. Dev. (submitted).

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

Sponsor: DOE - Office of Fossil Energy

KINETICS OF DESULFURIZATION OF HOT FUEL GAS WITH CALCIUM OXIDE. REACTION BETWEEN COS AND CaO

BNL - 24716

Ralph T. Yang and James M. Chen

Process Sciences Division

Rates of sorption of COS by CaO were measured in the temperature range of 500° to 900°C at a total pressure of 1 atm. The CaO sample was a reagent-grade fine powder with particle size of 1-5 μ. The overall rates in the temperature range of 600 to 900°C were correlated satisfactorily with the grain model (with a shape factor of 1.5) where chemical reaction was the rate-limiting step. The correlation with the grain model was also supported by the SEM observation of the physical structure of the CaO particles. Using the initial rates as the surface chemical rates, the temperature and concentration dependencies were determined and a rate expression was derived. The rate of sorption of COS by CaO was slightly higher than that of H_2S, using the literature data on the H_2S sorption. Significant sorption of COS takes place parallel to the sorption of H_2S in the coal gasification processes in which lime is used.

Yang, R. T. and Chen, J. M. Kinetics of Desulfurization of Hot Fuel Gas with Calcium Oxide. Reaction Between COS and CaO. Env. Sci. Tech. (in press).

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

Sponsor: DOE - Office of Fossil Energy

MODELLING AND KINETIC STUDIES OF A ROTARY KILN REACTOR: REGENERATION OF SORBENT FOR FLUIDIZED-BED COMBUSTION

BNL - 24731

James M. Chen and Ming-Shing Shen

Process Sciences Division

A kinetic study has been performed of the apparent solid-solid reaction between CaS and $CaSO_4$ with a rotary kiln reactor. The experimental conditions were within the range for regeneration of the lime-based sorbents for fluidized-bed combustion. A mathematical model has been derived for the rotary kiln reactor. The model interrelates the SO_2 concentration, as a function of distance and time, with the major operating variables of the reactor such as solid loading, temperature, gas flow rate, etc. A general first-order rate expression was used in the derivation. The theoretical values of the SO_2 concentration compared favorably with the experimental values, with the above three factors as the independent variables. The kinetic parameters of the chemical reaction extracted from the data obtained with the kiln reactor also compared favorably with those obtained directly and independently with a fixed-bed thermogravimetric reactor.

Chen, J. M. and Yang, R. T. Modelling and Kinetic Studies of a Rotary Kiln Reactor: Regeneration of Sorbent for Fluidized-Bed Combustion. Chem. Eng. Sci. (submitted).

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

Sponsor: DOE - Office of Fossil Energy

CALCIUM SILICATES - A NEW CLASS OF HIGHLY REGENERATIVE SORBENTS FOR HOT GAS DESULFURIZATION

BNL - 24785

Ralph T. Yang and Ming-Shing Shen

Process Sciences Division

A study has been conducted on the utilization of calcium silicates and the SiO_2-supported lime as regenerative sorbents for desulfurization of hot combustion gases. Except for γ-Ca_2SiO_4 and Ca_3SiO_5, all the calcium silicates and the SiO_2-supported CaO are equally or more reactive than CaO, and the regeneration rates of these sorbents are substantially higher than that of CaO.

Yang, R. T. and Shen, M. Calcium Silicates - A New Class of Highly Regenerative Sorbents for Hot Gas Desulfurization. AIChE Journal (submitted).

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

Sponsor: DOE - Office of Fossil Energy

REGENERATIVE PROCESS FOR DESULFURIZATION OF HIGH TEMPERATURE COMBUSTION AND FUEL GASES, PROGRESS REPORT NO. 7, OCTOBER 1-DECEMBER 31, 1977

BNL - 50809

R. T. Yang, A. S. Albanese, J. M. Chen, G. Farber, F. B. Kainz, J. Pruzansky, M-S. Shen, and M. Steinberg

Process Sciences Division

A method of pretreating limestone for enhancement of its utilization in fluidized-bed combustion has been found and is under further development. The method entails spraying of the stone with an aqueous solution of Fe^{++}/Fe^{+++} SO_3^{--}/SO_4^{--} before it is fed to the combustor. One percent of iron coated on the stone approximately doubles the rate of SO_2 sorption. Fe_2O_3 not only catalyzes the rate, but also enhances the sorption capacity of the stone.

The Brookhaven Regenerative Process, i.e., regenerating lime from sulfate with coal ash in a kiln-type reactor, is under further development. The results continue to show that a temperature of 1000°C is feasible for regeneration as compared with the temperature of 1100°C which is required by the fluidized-bed processes.

A commercial high-temperature insulation product containing primarily $CaSiO_3$ has been tested for SO_2 sorption. The rate and capacity were both higher than those of the reagent-grade $CaSiO_3$ although the reason for this effect is not established.

The mechanisms of the basic and common reactions taking place in the regeneration systems are being studied. It has been shown that gaseous intermediates do exist in the reaction system: $CaS + 3CaSO_4 \rightarrow 4CaO + 4SO_2$. Evidence has been gathered to show the occurrence of several other reactions between CaS and SO_2 and between CaO and SO_2 under the conditions common to the regeneration systems.

Coal ash has been found as a good binder to pelletize fine-sized sorbents. The iron oxide in the ash also acts as a catalyst for SO_2 sorption. The good binding property is attributed to the SiO_2 in the ash. Fine $CaCO_3$ pelletized with coal ash showed the catalytic effects. This method was suggested to and applied by Exxon investigators for pelletizing calcium aluminates cement powder with very good results.

Two conceptual AFBC process flow diagrams and corresponding mass and energy balances have been prepared. One flow sheet depicts a once through sorbent system (System I); the other, a regenerative system consisting primarily of an AFBC, a regenerator, and a sulfuric acid plant (System II). A process comparison of the two systems and a rough analysis of sulfuric acid market potential are also presented.

BNL Progress Report, October 1-December 31, 1977.

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

Sponsor: DOE - Office of Fossil Energy

REGENERATIVE PROCESS FOR DESULFURIZATION OF HIGH TEMPERATURE COMBUSTION AND FUEL GASES, QUARTERLY PROGRESS REPORT NO. 8, JANUARY 1-MARCH 31, 1978

BNL - 50866

R. T. Yang, A. S. Albanese, J. M. Chen, G. Farber, F. B. Kainz, J. Pruzansky, M-S. Shen, C. L. Steen, and M. Steinberg

Process Sciences Division

A highly reactive β-dicalcium silicate power sample has been acquired from Professor D. Roy of Pennsylvania State University. The sample was prepared by the Roy Evaporative Decomposition of Solution (EDS) process. We will use it in conjunction with our ash-binder pelletizing technique to form a highly regenerable and reactive sorbent for fluidized bed combustion. Other techniques for forming reactive silicates are also being studied.

Simplified mathematical models have been developed for kiln regeneration based on the data with a small quartz rotary kiln reactor. The model provides better understanding for scale-up of the promising Brookhaven Kiln Regeneration Process.

The Fe_2O_3 catalyzed sulfation and regeneration process has been further studied with a small quartz fluidized-bed sulfator and a small rotary kiln regenerator. Ten sulfation-regeneration cycles will be completed within the next reporting quarter. After completion of the cyclic experiments, we will make recommendations for field testing, i.e., testing in one of the DOE pilot fluidized bed combustors and regenerators.

The reactivity of a reconstructed $CaSO_4$ is indeed higher than the original sample. The reconstructed sample was made via the procedure:

$$CaSO_4 \xrightarrow{red.} CaS \xrightarrow{oxid.} CaSO_4.$$

We plan to further understand the morphological and structural changes taking place in the process.

A detailed analysis and a review of the high temperature $CaSO_4$ regenera-mechanism were made. All possible reactions in the system were taken into account. Rates of the more important (rapid) ones were measured. Existence of a gaseous intermediate indeed was ascertained and some mechanisms were proposed. Understanding of the mechanism will be useful in improving all the regeneration processes being developed.

Kinetics of the rapid reaction between CaO and SO_3 are being studied and the work will be completed shortly. This is part of our effort to understand the mechanism both in sulfation and regeneration.

A good attempt has been made to use ZnO as a regenerable sorbent for hot fuel gas desulfurization. The evaporation rate of the sorbent in a reducing atmosphere is too high for this sorbent to be of practical use.

BNL Quarterly Progress Report, January 1-March 31, 1978.

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

Sponsor: DOE - Office of Fossil Energy

REGENERATIVE PROCESS FOR DESULFURIZATION OF HIGH TEMPERATURE COMBUSTION AND FUEL GASES, QUARTERLY PROGRESS REPORT NO. 9, APRIL 1-JUNE 30, 1978

BNL - 50891

Ralph T. Yang, A. S. Albanese, J. M. Chen, G. Farber, F. B. Kainz, J. Pruzansky, M-S. Shen, and M. Steinberg

Process Sciences Division

Kinetic studies were performed on sulfation and regeneration of two $CaSiO_3$ samples, two β-Ca_2SiO_4 samples, a γ-Ca_2SiO_4 and a Ca_3SiO_5 sample. Except for the last two samples, the silicates showed higher overall rates and, more important, higher capacities for sulfation, as compared with CaO on a molar basis.

The rates of regeneration of the silicates were much higher than that of CaO. More specifically, the rates of thermal decomposition of the sulfated mono- and dicalcium silicates were about 15 times higher than that of the $CaSO_4$ which indicated the relative bond strengths between SO_3 and the sorbents.

X-ray diffraction and infrared analyses of the reaction products showed that: (1) SiO_2 and SO_4 are both chemically bonded to Ca in the sulfated $CaSiO_3$, (2) SiO_2 is not chemically bonded to $CaSO_4$ in the sulfated Ca_2SiO_4 and (3) the crystalline structures of both $CaSiO_3$ and $CaSiO_4$ are restored upon regeneration of the sulfated silicates.

Sulfation rates of $CaSiO_3$ and Ca_2SiO_4 are first order with respect to SO_2 only for $P_{SO_2} < 3000$ ppm of 1 atm. The activation energies for sulfation are, in the increasing order of the amount of SiO_2, 3.7 kcal (CaO), 5.4 kcal (Ca_2SiO_4) and 6.9 kcal ($CaSiO_3$).

Rates of sulfation and regeneration were measured for the SiO_2-supported CaO. CaO was precipitated on a high surface area granular SiO_2 from aqueous solutions of calcium salts followed by a heat treatment. Compared with the Al_2O_3-supported CaO, which were actually calcium aluminates on the surface of Al_2O_3, the sulfation rates were about the same but the regeneration rates were definitely higher for the SiO_2- supported sample.

A kinetic study has been performed on the apparent solid-solid reaction between CaS and $CaSO_4$ with a rotary kiln reactor. The experimental conditions are within the range for regeneration of the lime-based sorbents for fluidized-bed combustion. A mathematical model has been derived for the rotary kiln reactor. The model interrelates the SO_2 concentration, as a function of distance and time, with the major operating variables of the reactor such as solid loading, temperature, gas flow rate, etc.

Promising results were obtained on the utilization of coal ash as a binder for the fine-size sorbents such as the limestone dust and synthetic sorbents.

BNL Quarterly Progress Report, April 1-June 30, 1978.

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

Sponsor: DOE - Office of Fossil Energy

REGENERATIVE PROCESS FOR DESULFURIZATION OF HIGH TEMPERATURE COMBUSTION AND FUEL GASES, QUARTERLY PROGRESS REPORT NO. 10, JULY 1-SEPT. 30, 1978

BNL - 50944

A.S. Albanese, J.M. Chen, G. Farber, F.B. Kainz, J. Pruzansky, M-S. Shen
M. Steinberg

Process Sciences Division

A kinetic study has been performed with a rotary kiln reactor of the apparent solid-solid reaction between the sulfated limestone and the fly ash from a FBC. The experimental conditions were within the range for regeneration of the lime-based sorbents for fluidized-bed combustion. The measured SO_2 concentrations have been favorably interrelated with a derived mathematical model, with the major operating variables of the reactor such as solid loading, temperature, gas flow rate, etc. The kinetic parameters of the regeneration reaction, the maximum attainable SO_2 concentrations, and the effect of the molar ratio of C/S on the extent of $CaSO_4$ conversion to CaO have been obtained.

The sulfur sorption efficiency of the pellets of the limestone fines was found to be much higher than that of raw stone. Significant improvements in reducing the required Ca/S molar ratio in the FBC system could be achieved by using the pellets of the limestone fines to replace the raw stone sorbents. The effects of the compacting pressure and the ash content of the pellets on the sulfation rates and the degree of resistance to attrition were also measured.

Calcium silicates have been shown to have very favorable thermodynamic properties for regeneration. Equilibrium calculations were made for monocalcium silicate and dicalcium silicate and compared with calcium sulfate for thermal and reductive decomposition respectively. Calcium silicates produce much higher SO_2 levels during regeneration than limestone. Furthermore, calcium silicates have the advantage of not being "carbonated" in a CO_2 environment similar to that in pressurized fluidized-bed combustion of coal. It is therefore possible for cyclic use of these sorbents in a pressurized combustion system.

In contrast to limestones, β-dicalcium silicate retained its activity when repeatedly cycled between sulfation and regeneration. More reactive calcium silicates are being sought, as well as the means of forming them. Iron oxide has been shown to be catalyze the sorption of SO_2 by calcium silicates. The work on silica-supported lime will be continued. Much of the efforts are directed in finding a low cost macroporous silica support and increasing its calcium loading.

An economic comparison between an AFBC once-through limestone sorbent system and a kiln regeneration system has been made. Two alternative arrangements of the regeneration system were considered, one producing sulfuric acid from the SO_2 rich regenerator off-gas; the other, producing elemental sulfur.

A kiln reactor process for regenerating sulfated calcium oxide reduces the environmental impact of fluid bed waste disposal and improves natural resource utilization. Also, in consideration of the higher capital and operating costs for recovering liquid sulfur, a combined kiln regeneration/sulfuric acid process appears to be economically superior to a once-through sorbent and to a kiln regeneration/sulfur process, provided the acid can be sold within the vicinity of the power plant producing it.

BNL Quarterly Progress Report, July 1-September 30, 1978.

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

Sponsor: DOE - Office of Fossil Energy

POLYKETONES AND POLYSULFONES FOR CONSERVATION IN THE ETHYLENE POLYMER INDUSTRY, PROGRESS REPORT NO. 1, OCTOBER 1977-MARCH 1978

BNL - 50884

M. Steinberg, R. Johnson, P. Colombo, W. Cordes, M. Koral, and D. Goodman

Process Sciences Division

A series of ethylene-carbon monoxide copolymers have been prepared by chemical catalysis and Co-60 gamma radiation induction, ranging in carbon monoxide content from 41 to 49%. A correlation has been established between the method of preparation, the carbon monoxide content of the copolymers and the mechanical properties of the resulting products present evaluations indicate that copolymers containing $\sim$ 50% carbon monoxide prepared by Co-60 gamma induction have significantly improved mechanical properties over copolymers prepared by traditional chemical free-radical catalysis and which were found to contain < CO. Based on these results, it is suggested that further experimentation be conducted in radiation-induced copolymerization especially with the use of electron beam machines presently available to industry.

BNL Progress Report, October 1977-March 1978.

Program: Conservation in the Ethylene Polymer Industry-- Polyketones and Polysulfones

Sponsor: DOE - Office of Assistant Secretary Conservation and Solar Applications

POLYKETONES AND POLYSULFONES FOR CONSERVATION IN THE ETHYLENE POLYMER INDUSTRY, PROGRESS REPORT NO. 2, APRIL-SEPTEMBER 1978

BNL - 50955

Meyer Steinberg, Richard Johnson, William Cordes, and Donald Goodman

Process Sciences Division

A program is underway to investigate the substitution and introduction of CO and SO_2 into high molecular weight polymers of ethylene for the purpose of conserving ethylene feedstock for the polymer market. Et-CO polyketone copolymers, Et-SO_2 polysulfone copolymers and Et-CO-SO_2-terpolymers have been produced by Co-60 gamma radiation and by electron beam machine radiation. This is the first time that E-beam radiation has been used to produce these copolymers in high pressure systems. The yield for the 1:1 Et-CO polyketone copolymers appears to be square root dependent on the intensity. The electron machine radiation yields appear to be lower ($G = 10^2$ to 10^3) than that obtained with Co-60 gamma radiation ($G = 10^3$ to 10^4 or with bremstrahlung radiation produced by the electron beam interacting with the pressure vessel. The lower yields may be due to the high radiation intensity of the electron beam. The yield of Et-SO_2 polysulfone copolymer appears to be independent of radiation intensity and appears to be very high ($G = 10^4$ to 10^5) either with Co-60 or electron machine radiation. A strong post-irradiation polymerization effect is observed in the Et-SO_2 copolymer system. This is the first time an Et-CO-SO_2 copolymer has been reported especially with a content as low as 36 mole percent ethylene and 64 mole percent of combined CO and SO_2. The Et copolymers (1 to 1 Et-CO and 1 to 1 Et-SO_2 appear to be stable up to temperatures in the order of 275° to 300°C and the Et-CO copolymer has shown good tensile strengths. Much further characterization and formulation of the copolymer and terpolymer systems are needed to determine their market value.

BNL Progress Report, April-September 1978.

Program: Conservation in the Ethylene Polymer Industry--Polyketones and Polysulfones

Sponsor: DOE - Office of Assistant Secretary Conservation and Solar Applications

ENVIRONMENTAL CONTROL TECHNOLOGY FOR CARBON DIOXIDE

BNL - 24999

Meyer Steinberg, A.S. Albanese and Vi-Duong Dang

Process Sciences Division

The possible adverse global environmental effects of CO_2 buildup in the atmosphere due to emissions from increasing fossil fuel combustion operations, have prompted an investigation of a number of possible methods and systems for controlling CO_2 emissions and buildup. A systematic overview is presented of a number of routes for removal, recovery, disposal, and reuse of CO_2 from various control points in the global system. The energy and mass balances for various routes are used as a criteria for evaluation. An assessment of the value of alternative energy sources as a means of CO_2 control is made.

Steinberg, M., Albanese, A., and Dang, V. D. Environmental Control Technology for Carbon Dioxide. Presented at 71st Annual Meeting of American Institute of Chemical Engineers, Miami, Florida, November 12-16, 1978.

Program: Environmental Control Technologies (1) FHP of Coal and (2) Atmospheric CO_2 Control

Sponsor: DOE - Office of Environmental Control Technology

ENVIRONMENTAL CONTROL TECHNOLOGY FOR THE FLASH HYDROPYROLYSIS OF COAL, PROGRESS REPORT NO. 1, JUNE 20, 1977 TO SEPTEMBER 30, 1977

BNL - 50793

Meyer Steinberg and Anthony S. Albanese

Process Sciences Division

The subject program pertains to the assessment and control of potential pollutants from Brookhaven National Laboratory's Flash Hydropyrolysis of Coal Process (FHP) and from related coal liquefaction processes currently under development at Rocketdyne, Cities Service, IGT and CCNY. Data obtained from the experimental FHP unit currently in operation at BNL will provide the primary basis for our analysis; however, we will attempt to extend and generalize our findings and conclusions by reviewing and analyzing the available literature and data on the related processes identified above. Common problem areas and applicable technology will be identified as well as significant differences in effluents and required control technologies. The overall objective of the program is to generate data and information essential for the application of coal liquefaction processes to industrial systems.

This report presents information on: (1) the polynuclear aromatic hydrocarbons contained in the organic phase of the FHP liquid product, (2) the carbon, hydrogen, nitrogen, sulfur, and trace elements content of the FHP organic liquid product, (3) the elemental composition of coal and char obtained from the FHP unit, (4) the volatile matter contained in the coal feed and FHP char product, and (5) a conceptual process flow plan for a FHP-Chemical complex (including material balance).

BNL Progress Report, June 20, 1977-September 30, 1977.

Program: Environmental Control Technologies (1) FHP of Coal and
(2) Atmospheric CO_2 Control

Sponsor: DOE - Office of Environmental Control Technology

ENVIRONMENTAL CONTROL TECHNOLOGY FOR ATMOSPHERIC CARBON DIOXIDE, QUARTERLY PROGRESS REPORT NO. 1, JUNE 20, 1977 TO SEPTEMBER 30, 1977

BNL - 50794

Meyer Steinberg, Anthony S. Albanese, and V. D. Dang

Process Sciences Division

The primary objective of the subject program is to assess the potential options for controlling atmospheric CO_2. Accordingly, CO_2 control scenarios based on conventional technology and applied to the larger industrial emitters will be prepared. The studies will include preliminary cost estimates of selected processes, to identify fruitful areas for environmental control technology (ECT) programmatic development as related to CO_2 release and control. BNL's prior experience in this area includes the development and evaluation of a number of processes for removing CO_2 from the atmosphere for the purpose of producing synthetic carbonaceous fuels including methanol, gasoline, and methane. Background information from other DOE programs will be used to determine the limitations for the control studies.

This progress report presents background information on: (1) the concentration levels of CO_2 in the atmosphere during the last one hundred years; (2) the possible effects of rising CO_2 levels; (3) the impact of fossil fuel use in the United States on overall worldwide CO_2 emissions; (4) the impact of increased coal utilization on CO_2 emissions; and (5) the process considerations for controlling CO_2.

BNL Quarterly Progress Report, June 20, 1977-September 30, 1977.

Program: Environmental Control Technologies (1) FHP of Coal and (2) Atmospheric CO_2 Control

Sponsor: DOE - Office of Environmental Control Technology

ENVIRONMENTAL CONTROL TECHNOLOGY FOR ATMOSPHERIC CARBON DIOXIDE, PROGRESS REPORT NO. 2, OCTOBER 1, 1977 TO MARCH 31, 1978

BNL - 50877

Meyer Steinberg and Anthony S. Albanese

Process Sciences Division

A methodology for systematically constructing and evaluating scenarios for controlling atmospheric carbon dioxide is described. Based on fundamental principles and on a search of the literature a number of alternative processes (building blocks), ranging from conventional technologies to advanced concepts, are presented for consideration in the construction of these scenarios. Since there are several key factors to consider in evaluating alternative control strategies, such as, energy requirements, disposal options and process inefficiencies, each of which could render a particular alternative impracticable, a reasonably thorough analysis of each candidate scenario is required before meaningful conclusions can be reached.

This progress report presents information on (1) a logic structure for constructing scenarios, (2) process options for CO_2 capture, reuse and disposal, (3) a methodology for evaluating scenarios, (4) an assessment of the energy requirements for capturing CO_2 from the atmosphere, and (5) an evaluation of a control system for removing CO_2 from power plant stack gases by absorption with seawater, followed by deep ocean disposal.

BNL Progress Report, October 1, 1977-March 31, 1978.

Program: Environmental Control Technologies (1) FHP of Coal and (2) Atmospheric CO_2 Control

Sponsor: DOE - Office of Environmental Control Technology

ENVIRONMENTAL CONTROL TECHNOLOGY FOR THE FLASH HYDROPYROLYSIS OF COAL, QUARTERLY REPORT NO. 2, OCTOBER 1, 1977 TO MARCH 31, 1977

BNL - 50906

Meyer Steinberg and Anthony S. Albanese

Process Sciences Division

Product streams of the experimental Flash Hydropyrolysis (FHP) unit currently in operation at Brookhaven National Laboratory have been analyzed for sulfur, nitrogen, phenol and other potential pollutants. Based on experimental results and analytical studies, a preliminary environmental assessment of a conceptual, industrial scale FHP-Chemical Complex producing pipeline gas, benzene, light oils, ethylene and a number of byproducts has been made. Solid, liquid and gaseous effluents of the complex have been evaluated, and required effluent treatment facilities and potential problem areas identified.

BNL Quarterly Report, October 1, 1977-March 31, 1977.

Program: Environmental Control Technologies (1) FHP of Coal and (2) Atmospheric CO_2 Control

Sponsor: DOE - Environmental Control Technology Division

ENCAPSULATION OF PHASE CHANGE MATERIALS IN CONCRETE MASONRY CONSTRUCTION, PROGRESS REPORT NO. 1, AUGUST 1977-FEBRUARY 1978

BNL - 50827

M. J. Sansone and W. Horn

Process Sciences Division

Work performed at Brookhaven National Laboratory on Union Carbide Nuclear Division, ORNL Number 19Y-14279V, "Encapsulation of Phase Change Materials in Concrete Masonry Construction", is summarized in this First Quarterly Report for the period ending February 1978. The improvement of thermal energy storage capacity of potential building materials by incorporation of phase change materials (PCM's) is being explored. Both inorganic salt hydrides and organic systems are potentially useful PCM's for encapsulation in concrete, polymer concrete, and/or polymer-impregnated concrete matrices. It is felt at this time that most PCM's melting at or above 40°C can be encapsulated in large quantities in polymer concrete. Methods relating to the encapsulation of lower melting materials in various matrices are currently being studied.

BNL Progress Report, August 1977-February 1978.

Program: Encapsulation of Phase Change Materials in Concrete Masonry Construction

Sponsor: DOE - Office of Energy Storage Systems via subcontract from ORNL

ENCAPSULATION OF PHASE CHANGE MATERIALS IN CONCRETE MASONRY CONSTRUCTION, PROGRESS REPORT NO. 2, MARCH 1978 TO MAY 1978

BNL - 50896

M. J. Sansone, T. Sugama, and W. Horn

Process Sciences Division

Work performed at Brookhaven National Laboratory on Union Carbide Nuclear Division, ORNL order number 19Y-14279V, "Encapsulation of Phase Change Materials in Concrete Masonry Construction", is summarized in this Second Progress Report for the period of March 1978 to May 1978. The improvement of phase change materials (PCM's) has been demonstrated by thermal measurements. Thermal analysis of PCM's is continuing in order to identify the most promising systems. Particular attention is being focused on polyethylene glycols and $MgCl_2$-$CaCl_2$ H_2O eutectic systems although other materials are still under consideration. Efforts to encapsulate phase change materials in porous aggregate are continuing. Non-leaking coatings for the aggregate and for the PCM matrix materials are under development. Thermal analysis capabilities have been established and include DSC, TGA, a thermal comparator for conductivity measurements, and a heat-flow calorimeter for heat capacity measurements on large samples. Thermal measurements on PCM composite materials are continuing.

BNL Progress Report, March-May 1978.

Program: Encapsulation of Phase Change Materials in Concrete Masonry Construction

Sponsor: DOE - Energy Storage Systems via subcontract from ORNL

LOW PECLET NUMBER HEAT TRANSFER FOR POWER-LAW NON-NEWTONIAN FLUID WIT. HEAT GENERATION

BNL - 24806

Vi-Duong Dang

Process Sciences Division

Heat transfer for power-law non-Newtonian fluid with heat generation and axial conduction is analyzed. Radical and axial temperature distribution and the Nusselt number inside a tube are obtained in terms of nonorthogonal series expansion. Eigenvalues and eigenfunctions are given for different values of various parameters. The effects of Peclet number, power-law model index, viscous dissipation, and heat generation on the temperature distribution and Nusselt number are discussed. Comparison of the present results for extreme cases with those obtained by previous workers shows good agreement.

Dang, V. D. Low Peclet Number Heat Transfer for Power-Law Non-Newtonian Fluid with Heat Generation. J. Appl. Polymer Sci. (submitted).

Program: General

Sponsor: DOE

THERMOELECTROCHEMICAL CYCLES FOR POWER AND HYDROGEN PRODUCTION

BNL - 24387

Meyer Steinberg

Process Sciences Division

Based on electrochemical mechanisms, a new power cycle for converting thermal to electrical energy is presented. The cycle is referred to as the thermoelectrochemical (TEC) power cycle. The general principle involves combining the electrochemical decomposition of a compound to its elements at a condition where the free energy change is low with the recombination of the same or a different compound from its elements at a condition where the free energy change is high. The difference in free energies gives a net difference in electromotive force which results in a net power output for the system. The power cycle combines the operation of an electrolyzer at a high temperature, low emf condition, with a fuel cell at a low temperature high emf condition. The thermal energy is used to provide the high level heat in the electrolyzer while the low level heat is rejected in the fuel cell. Heat is thus converted to DC electricity. Ideal power cycle efficiencies are equal to the Carnot efficiency for non-condensing systems. The principles are illustrated with a H_2-O_2-H_2O system and with a H_2-O_2-Cl_2-HCl system. In the H_2-O_2-H_2O system, utilizing heat at 727°C (1000°K) in the electrolytic cell and rejecting heat at 25°C (298°K) in the fuel cell, results in a net ideal emf difference of 0.187 volts with a Carnot cycle efficiency of 70%. The system could be directed towards application of nuclear heat from high temperature gas cooled reactors or at still higher temperatures from coal, oil, or gas fired plants where efficiencies could reach over 80%. Overvoltage and cell IR losses will reduce these ideal efficiencies, however, the potential for improvement over existing cycles appears to be very high. A feasible system, minimizing overvoltage losses in the electrolytic cells appears to be the operation of a cycle in which water is first electrolyzed at 1000°K (727°C) to H_2 and O_2. The H_2 is then fed to a fuel cell where it combines with Cl_2 at 298°K (25°C) forming aqueous HCl. The aqueous HCl is oxidized with the O_2 from the electrolyzer back to water and Cl_2, thus, closing the cycle. The net cell voltage is calculated to be 0.362 volts and efficiencies approaching the Rankine cycle efficiency of 47.2% could be obtained. Other cycles are described. The benefits of the TEC cycle is that it produces electricity from thermal energy with no moving parts and at moderate pressures, potentially making this system mechanically a highly reliable one. The high temperature material stability problem must be balanced against the increased thermal efficiency of the power cycle. TEC may have especially suitable applications for the production of electrometals, (Al and Cu), electrochemicals and synthetic fuels because of the direct use of the DC current generated in the cycle. It is recommended that these systems be further developed and evaluated.

Steinberg, M. Thermoelectrochemical Cycles for Power and Hydrogen Production. Presented at 2nd World Hydrogen Energy Conference, Zurich, Switzerland, August, 21-24, 1978.

Program: Synthetic Fuels Development

Sponsor: DOE - Office of Magnetic Fusion Energy

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