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Nuclear Engineering Department

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*AEC budget activity numbers.

SUMMARY

Introduction

The Nuclear Engineering Department's program can be divided into three categories. The first is basic research, which encompasses fundamental studies in reactor physics, chemistry, and metallurgy. Studies are also being carried out on reactor materials at high temperatures, fission product release, liquid-metal heat transfer, and superconductivity in metals.

In the second category is the long-range work of developing components that may bring about significant advances in reactor technology and radiation application. Some of the more important phases of this work are the development of reactor fuels, utilization of fluidized beds for water desalination, radiation engineering methods, waste processing devices, and direct conversion concepts.

The engineering and evaluation studies, the third category, are focused on practical application of the work in the preceding categories. Engineering design and development work is being carried out on a pulsed fast reactor to be used as a source of neutrons for basic research in physics and chemistry. Typical studies that continued during the year concerned fast reactors and chemonuclear reactors. Assistance was given to the Division of Reactor Development and Technology of the Atomic Energy Commission in the updating of earlier US AEC Reports to the President on Civilian Nuclear Power.

At his own request O.E. Dwyer was relieved as head of the Chemistry and Chemical Engineering Division so that he could devote his time to research and writing in the field of heat transfer. R.H. Wiswall, Jr., was appointed head of the new Chemistry Division. The chemical engineering activities (heat transfer under O.E. Dwyer, chemical technology under L.P. Hatch, and safety studies under A.W. Castleman) were combined with the present Engineering Division. T.V. Sheehan continues as Head of this Division, J. M. Hendrie is the Associate Head, and R. J. Isler continues as Assistant Head.

The heat transfer group of the Engineering Division has continued publication of the *High Temperature Liquid-Metal Technology Review* for the fifth year.

O.E. Dwyer was invited to author a chapter on liquid-metal heat transfer for the new edition of the *Liquid-Metals Handbook*.

T.V. Sheehan was elected a fellow in the American Society of Mechanical Engineers.

A new activity in the department called the National Neutron Cross Section Center (NNCSC) was formed by merging the Neutron Cross Section Compilation Center (Sigma Center) and the Cross Section Evaluation Center. The original Centers operated within the Reactor Physics Division of the Department.

J. J. Dorning was the winner of the Mark Mills Award of the American Nuclear Society for outstanding graduate work in Nuclear Science and Engineering. He did his research at BNL while enrolled at Columbia University.

J. Chernick participated in a joint India-USA study on the economics of nuclear power for India. The initial studies were carried out in Bombay, India, during the period March-April 1967.

J. J. Dorning, P.A. Michael, and M.N. Moore (summer visiting physicist) presented papers at the IAEA Symposium on Neutron Thermalization and Reactor Spectra held at Ann Arbor, Michigan, July 17-21, 1967.

L. Shotkin presented a paper at the Symposium on Two-Phase Flow Dynamics held September 4-9, 1967, at the Technological University in Eindhoven, Netherlands.

P.A. Michael presented a paper at a seminar sponsored by the Advisory Group for Aerospace Research and Development, NATO, at Teddington, England, September 18-21, 1967.

L. Shotkin has completed his term as a member of the Executive Committee for the Reactor Physics Division of the American Nuclear Society.

Several seminars at universities were presented by staff members: R. Goldstein and M.M. Levine, University of Florida; P.A. Michael, Notre Dame

and Illinois Institute of Technology; L. Shotkin, Columbia University; J. Chernick and R.L. Hellens, Rensselaer Polytechnic Institute.

R. Goldstein, L. Shotkin, J. Chernick, N. Corngold, E.V. Weinstock, C. Sastre, and G.C. Pomraning (summer visiting physicist) presented papers at the Conference on Research Reactor Utilization and Reactor Mathematics sponsored by the American Nuclear Society and Comisión Nacional de Energía Nuclear of Mexico, at Mexico City, May 2-4, 1967.

H.J.C. Kouts participated in a team visit to European laboratories which led to a comprehensive report on the status of fast reactor physics in Europe. He also participated in a study group meeting on research reactor utilization held in Japan.

G. Price spent a month at the Bhabha Atomic Research Centre in Trombay, India, as an advisor to the India Atomic Energy Commission on the development of their experimental reactor physics program.

R.L. Hellens presented a paper on inferences from graphite and light water critical experiment analyses, and P.F. Palmedo presented a paper on anisotropic neutron migration at the Joint International Conference on the Physics of Reactor Design held in London, England, June 1967.

The FS-1 critical experiment was first brought to criticality on October 31, 1967, under the supervision of K.W. Downes and A.J. Court. This is the first fast critical experiment to be conducted at BNL and will be used to study the physics of fast reactors.

B.R. Sehgal prepared a paper for the EACRP Tokyo meeting in October 1967 entitled Brookhaven U^{233} - ThO_2 Thermal Lattice Experiments.

D. Ballantine is on leave with the Division of Isotopes Development, AEC, Washington, D.C.

D.J. Metz gave a series of lectures in connection with the USAEC Atoms At Work Exhibit in Ankara, Turkey.

G. Adler gave a series of lectures on radiation effects on organic crystals at the University of Pavia, Italy, the Weizmann Institute, Israel, the Middle East Technical University, Turkey, and Democritus Institute, Greece.

B. Manowitz presented an invited paper entitled Review of Industrial Radiation Chemistry in the United States at a joint British Nuclear Energy Society-British Nuclear Forum Symposium in London, England.

M. Steinberg served on the first IAEA Panel on Radiation Chemistry and Technology in Vienna, Austria.

J.H. Cusack presented a paper at the Japan Atomic Forum, conducted negotiations with representatives of the Japan AEC on the Brookhaven-Takasaki Exchange Information Program, and made final on-site arrangements for research irradiators to be sent to India and Pakistan by BNL at the request of the AEC.

Dr. Antonio Faucitano and Dr. Angelo Perotti, guest scientists from the University of Pavia, Italy, concluded their stay at BNL. While at BNL they worked with G. Adler on radiation effects on organic crystals.

Three guest scientists arrived during the year: K. Krishnamurthy (India AEC), working with J.H. Cusack on radiation engineering; Shoichi Sato (University of Tokyo) working on chemonuclear research with M. Steinberg; and R. Gabarain (Argentina AEC) working on polymer chemistry with M. Steinberg.

L.G. Stang, Jr., continued as Editor of *Nuclear Applications*, a journal of the American Nuclear Society, now in its third year of publication.

The following is a list of papers that were presented by invitation of the sponsors of the respective meetings. M. Hillman and A.J. Weiss, Chemical effects of decay of Te^{129m} in aqueous solution, International Hot-Atom Chemistry Symposium, Kyoto, Japan, October 11-13, 1967; P. Richards, Radioisotope generators for clinical use, Am. Med. Assoc. Meeting, Atlantic City, June 19, 1967; P. Richards, Radionuclide milking systems, 8th Japan Conf. Radioisotopes, Tokyo, November 13-16, 1967; P. Richards and H.L. Atkins, Technetium-99m labeled compounds, 7th Ann. Meeting Japanese Soc. Nuclear Medicine, Tokyo, November 17-18, 1967.

S. Feldberg was invited to prepare a chapter, entitled Digital simulation. A general method for solving electrochemical diffusion-kinetic problems, for Vol. 3, *Electroanalytical Chemistry. A Series of Advances*, a series of books edited by A.J. Bard and published by M. Dekker.

C. Auerbach was named Editor of *Chemical Instrumentation*, a journal to be published by M. Dekker beginning in 1968.

With the transfer to private industry of the production and distribution of Sr^{87m} generators, BNL has now withdrawn from the routine production of all special isotopes except for Mg^{28} . This frees

personnel to concentrate on the more important function of developing medical applications of isotopes.

D.H. Gurinsky was invited to participate in the ceremonies celebrating the 25th anniversary of the first self-sustained nuclear fission in Chicago, November 1967.

J.R. Weeks participated on the U.S. team for the U.S.-U.K. Libby-Cockroft exchange on reactor corrosion, as the sole U.S. representative concerned primarily with liquid-metal-cooled reactors, in April 1967 at AERE, Harwell, England.

J. Sadofsky was elected Chairman of the AEC Electron Microprobe Users Group at its 2nd annual meeting at the Somerset Hotel in Boston, June 13, 1967. He was also Chairman of the 21st AEC Metallography Group Meeting held at Brookhaven on May 10-12, 1967.

The proceedings of the International Conference on the Properties of Liquid Metals held at Brookhaven in 1966 were edited by P.D. Adams, H.A. Davies, and S.G. Epstein and were published by Taylor and Francis, Ltd., London.

J.M. Galligan was invited to attend a NATO meeting in Norway and other scientific meetings in Japan and Texas.

In September 1967, S. Epstein presented an invited seminar on electromigration in liquid alloys at Syracuse University.

Reactor Physics Division

(04-40-01-02-1)

Work in theoretical reactor physics continued during 1967 in the areas of reactor analysis, basic and applied theoretical reactor physics, and neutron cross section compilation and evaluation. In September the last activities were merged into a new and enlarged National Neutron Cross Section Center with division status; the work of this Center is therefore reported elsewhere. Emphasis of the theoretical work was shifted to fast reactor problems in support of the LMFBR program. In addition, a task force was formed to aid the Division of Reactor Licensing on reactor physics problems related to the licensing of U.S. power reactors.

Work in reactor analysis was confined to two general areas: (1) the development of a reliable lattice analysis code, and (2) the study of leakage effects in small assemblies.

Most of the effort was devoted to improvement and testing of the HAMMER lattice analysis code so that it can be used with confidence in evaluating the ENDF/B cross section data by comparison with integral experiments. By incorporating resonance shielding and overlap corrections, inferred from Monte Carlo and embodied in a correlation formula, the HAMMER code is capable of predicting lattice reaction rates which are in excellent agreement with the Bettis RECAP code. The latter uses the Monte Carlo method entirely from fission to absorption and is presumably exact, although very expensive in computer time. The testing of HAMMER against integral measurements was continued with the analysis of the British BICEP exponentials, the BNL graphite criticals, the BNL Th-U²³³ exponentials, and the B&W spectrum shift criticals.

The proper treatment of neutron leakage is central to the satisfactory analysis of both fast and thermal neutron experiments, since most of these assemblies are small. Even in thermal systems the principal error seems to lie in the worth of reflected fast neutrons and this case was studied first because a large amount of BNL experimental data bears on the problem. Multigroup DSN calculations show a trend that is similar to that inferred from experiments, while few-group DSN calculations show similar but probably exaggerated effects. An attempt is being made to understand the source of these differences between experiment and the various theoretical descriptions of the problem.

On the applied side, research in the Theoretical Reactor Physics Group involved problems in code development, reactor safety, and analysis of fast criticals and other fast spectrum assemblies. Work was initiated on other problems at the behest of the Division of Reactor Licensing.

On the basic side, research in the Theoretical Reactor Physics Group centered on the theory of transient and asymptotic experiments, mathematical methods, calculation of resonance absorption, reactor kinetics, and fluid dynamics.

A rather complete analysis of the pulsed neutron experiment in small light water systems was completed. The effect of various scattering models and of the degree of scattering anisotropy upon calculated decay constants was studied. The results indicated that scattering anisotropy must be included, though in a wide range the use of transport corrected total cross sections is an adequate approximation. It was also shown that the hydro-

gen in the water must be considered to be bound but that the most sophisticated models are not essential. In another study a comparison of the theoretical description of the neutron wave experiment and the pulsed neutron experiment showed that both experiments yield the same information.

A generalized perturbation approach to non-linear space-independent reactor kinetics was developed. This method, which is especially applicable to reactor safety studies, is such that its application is straightforward and does not require the special insight and experience that other methods sometimes require. It was also extended to space-dependent systems. Other work included a review of reactor excursion models and an improvement of the expansion method for the calculation of the zero-power describing function.

It was found that an improved iteration procedure for the application of the intermediate resonance formula for the calculation of resonance absorption yields a more rapidly convergent series and improved accuracy. A mathematical study on a rational method of choosing the unperturbed operator in a perturbation expansion was applied to resonance absorption in such a way that estimates of the upper and lower bounds of the exact resonance integral could be made.

In fluid dynamics, previous work on the two-phase flow of boiling water is being extended to take into account the special problems that arise in liquid-metal systems. Development work is continuing on methods of obtaining numerical solutions of the time-dependent Navier-Stokes equations. Recent work has been focused on the problem of accuracy and stability of the numerical solutions and the inclusion of realistic body forces on bodies that accelerate in a viscous fluid.

At the end of the year, almost all activities in experimental reactor physics were shifted to support the AEC's program to develop a Liquid Metal Fast Breeder Reactor. The final experiments on thermal reactors were completed in 1967. These included a series of exponential experiments with $U^{233}O_2$ - $Th^{232}O_2$ rods in light water and a final analysis of the data from critical experiments conducted with semihomogeneous mixtures of U^{235} and graphite. A set of studies of anisotropic neutron diffusion in lattices of slabs of aluminum and water was also completed; the results of these experiments should provide useful tests of ability to calculate effects of this phenomenon in all reactors, thermal as well as fast.

The research in support of development of a fast breeder reactor was centered on the use of a fast critical assembly whose construction was completed early in the year. Operation of the assembly was delayed during writing of a Facility Safety Analysis Report to justify the use of new operating limits, and a Safety Report on the experiments to be performed with the assembly. These reports are now complete and have been approved, together with the revised operating limits; the loading to critical of the first assembly was begun.

In the meantime, preparation for the experiments continued. A program was conducted to investigate the behavior of proton recoil counters used in measurements of fast neutron spectra, to eliminate sources of error, and to improve resolution to the point theoretically attainable. These studies revealed the need for care in fabricating the central collector wire and in purifying the filling gas. When proper care is taken in these respects, the resolution is seen to be as good as any that have been reported. Improved methods of analyzing the data obtained with such counters were also developed.

Other studies were directed toward the improvement of methods of measuring spatial distributions of reactions in fast reactors, particularly of fissions. Preparations are being made to use these techniques in cells inserted in the fast critical assembly.

A by-product of certain pulsed neutron experiments for development of a pulsed reactor was discovered that casts doubts on the correctness of most pulsed neutron experiments. It was found that when the neutron detector is located outside the moderator, the measured decay time depends on the distance to the detector.

National Neutron Cross Section Center (04-40-01-03-1, 05-03-01-03-0)

The cross section activities formerly within the Neutron Cross Section Compilation Center (Sigma Center) and the Cross Section Evaluation Center were consolidated into the National Neutron Cross Section Center in order to realize greater efficacy as an information center.

The publication of supplements to the second edition of *Neutron Cross Sections* (BNL 325) was completed. The updating of the SCISRS tape with new and old data continued. A newsletter was

issued that consisted of a reference and bibliography index and isotope sort that pertained to data contained in the SCISRS library.

The Evaluated Nuclear Data File was substantially augmented by contributions of the Cross Section Evaluation Working Group. Data for 42 materials were released to USA laboratories and European Nuclear Energy Agency countries. These data are complete in what is needed for reactor calculations.

Cross section analysis work continued in the areas of cross section statistics and cross section fitting techniques. Optical model parameters were obtained that produced good fits to the 1.0-MeV scattering data from the lead isotopes 206, 207, and 208. Final results of the multilevel fitting of the total and fission cross section of U^{235} below 37 eV were published. The multilevel fitting of the cross sections of nonfissile elements continued.

Evaluation and Technical Assistance Group (04-01-91-01-1)

The Evaluation and Technical Assistance Group continued to assist the AEC in the areas of program review and the evaluation of specific reactor concepts. Seven of the program plans for the Liquid-Metal Fast Breeder Reactor Program Office were reviewed at the request of the Division of Reactor Development and Technology (RDT); these were the sections on components, instrumentation and control, sodium technology, core design, fuel recycle, physics, and safety. The drafts of reports on evaluations performed by the AEC's light water and advanced converter task forces were examined as part of BNL's participation in the current civilian nuclear power studies.

In connection with those studies, BNL personnel constitute the working group of the thorium systems task force and, as such, have evaluated the technical and economic potential of the molten salt breeder reactor. In addition, an assessment of the role of thorium in the U.S. civilian nuclear power economy was completed. The results of these two studies were submitted to RDT in report form. Members of the Evaluation and Technical Assistance Group also served on the systems analysis task force and the advanced converter task force.

Assistance on NED-sponsored efforts involved completion of static screening tests on refractory metals and fuel specimens in nitrogen at 1930°C (3500°F) at the General Electric Company's Nuclear Materials and Propulsion Operation. Also, multigroup, diffusion-theory computations were made to ascertain the safety effects following the loss of one steel bar in the anticritical grid of the HFBR.

In accordance with an agreement between the Indian AEC and the USAEC, BNL is participating in a joint India-USA study of the viability of nuclear power in the Indian economy. The commitments include the release of evaluated technical and economic data on the molten salt breeder reactor and estimates of the capital cost of sodium-cooled fast breeder reactors in the power range of 150 to 1000 MW(e).

Chemistry Division (05-05-03-00-0)

The electrical double layer that exists at a charged surface in a fused salt is interesting both for its own sake and because it must be understood in order to interpret electrode reactions. A program was started in which the double layer is being investigated by means of capacitance measurements on a dropping bismuth electrode in a chloride melt. Preliminary measurements showed no frequency dispersion of capacitance; this is in disagreement with a report in the Russian literature.

The determination of transference numbers in molten salt mixtures as a function of concentration was continued and extended to the system $LiCl-CdCl_2$. Also continued was the galvanic-cell determination of free energy of mixing in fused salts over a concentration range; $LiCl-CeCl_3$ and $KCl-CeCl_3$ were covered.

The solubility of chlorine in three molten salts was determined as a function of temperature. From these data, heats of solution were determined as follows: in $PbCl_2$, $\Delta H = 9.4$ kcal/mole Cl_2 ; in $LiCl-KCl$ eutectic, $\Delta H = 3.7$ kcal/mole Cl_2 .

The mechanism by which a platinum electrode becomes more active when it is given alternate anodic and cathodic treatments was studied in experiments in which the chief variable was the purity of the electrolyte. The application of very rigorous purification procedures had a marked effect on electrode behavior. From a quantitative

study of the relationships it was inferred that the activation treatment owes its effectiveness to its action in removing adsorbed contaminants from the electrode surface.

Of all the alloy-hydrogen systems investigated so far, $\text{Mg}_2\text{Ni-H}_2$ and $\text{Mg}_2\text{Cu-H}_2$ seem best suited to the storage of hydrogen for later use as a fuel. An investigation of the pressure-composition-temperature relationships in these systems showed that the reactions involved are probably $\text{Mg}_2\text{Ni} + 2\text{H}_2 \rightarrow \text{Mg}_2\text{NiH}_4$ and $2\text{Mg}_2\text{Cu} + 3\text{H}_2 \rightarrow 3\text{MgH}_2 + \text{MgCu}_2$. Values of ΔH , ΔF , and ΔS have been obtained for each reaction. Equilibrium was reached much faster in these reactions than with Mg alone, and a rough measure of the first-order rate constant showed that the decomposition of Mg_2NiH_4 proceeded at a high enough rate, at 240°C , to make it of practical interest as a source of supply for a combustion engine or fuel cell. The addition of small amounts of Cu or of Ni were found to have a catalytic effect on the reaction between Mg and H_2 .

The thermal stability of perfluorobicyclohexyl was found to be orders of magnitude less than that of some other fluorocarbons, so a detailed kinetic study of its decomposition was undertaken. The reaction was found to be first order, homogeneous, and not to involve a chain. The activation energy is 73 kilocalories. The main reaction products were identified and from their relative abundance certain reaction paths involving postulated free-radical intermediates were deduced.

A number of stable ion radicals were prepared from cyclic organic compounds by treating them, in solution, with strong oxidizing or reducing agents. Since such radicals can be studied by ESR as well as absorption spectroscopy, they lend themselves well to structure determinations; and such determinations are in turn valuable in kinetic theory. From studies of certain diazole derivatives containing a sulfur or a selenium atom in the ring, it was concluded that a theoretical model which employs only the p -orbitals of the heteroatom satisfactorily accounts for the observed spectral data.

The preparation and behavior of perfluoro-Dewar benzene and its derivatives were studied, both for comparison with the corresponding hydrocarbons and with regard to their possible role as reaction intermediates. A new compound, perfluoro-Dewar xylene, resulted from this work; and an as yet unidentified isomer of C_6F_6 was produced by the irradiation of perfluoro-Dewar benzene.

The mechanism and the products of the reaction between graphite and hydrogen were investigated at temperatures up to 3500°K and over a wide range of gas pressure. Acetylene is the main product, and at pressures below 0.01 atm H_2 it accounts for $>99\%$ of the hydrocarbons found. This is consistent with spectroscopic evidence that C_2 is the predominant vaporizing species. The vapor adjacent to a graphite surface at 3200° to 3450°K was examined by both emission and absorption spectroscopy and a value of 214.5 kcal/mole for the heat of sublimation of C_2 was obtained.

Radiation Division

(04-40-04-03-1, 05-05-03-00-0, 08-03-02-00-0,
08-04-00-00-0, 08-05-00-00-0)

The radiation research effort is mainly concerned with the mechanisms of radiation-induced reactions in organic solids and liquids and in simple inorganic compounds.

The postirradiation reactions of propionamide, n -butyramide and iso-butyramide with oxygen, nitric oxide, sulfur dioxide, and ethylene have been studied by using gas absorption, ESR, x-ray diffraction, and product analysis. Radiolysis of acetonitrile has shown that very little nitrogen is formed, and there is no evidence for formation of any azo intermediates. The radiation-induced ionic polymerization of styrene and α -methylstyrene as a function of temperature indicates the operation of several competing processes. The radiolysis of gases absorbed on solids is characterized by an efficient transfer of energy from the bulk solid to the adsorbed phase. The deposition of fission fragment energy in nitrogen over the entire track has been studied. Also under investigation is the radiolysis of N_2O near its critical temperature as a function of gas density and the formation of ozone from oxygen.

The radiation processing effort is directed toward the use of nuclear energy for the production of industrial chemicals.

The construction of the Chemonuclear In-Pile Research Loop (CIRL) is essentially complete.

Data have been obtained in nitrogen fixation by irradiating gaseous $\text{N}_2\text{-O}_2$ bubbling through aqueous media. This apparently leads to much higher G -values than have been measured before for the $\text{O}_2\text{-N}_2$ system.

Because of the increase in industrial interest, studies of the radiation-induced polymerization of ethylene are being carried out at a reduced rate.

Studies with the cooperation of the U.S. Bureau of Reclamation have shown that radiation- and chemical-initiator-produced concrete-polymer materials have markedly improved strength, resistance to abrasion, and resistance to freeze-thaw attack as compared with ordinary concrete.

The possible use of ionizing radiation for the oxidation and removal of ferrous iron from acid mine drainage is being investigated.

The radiation engineering effort is concerned with problems of engineering processes and process equipment of which radiation is an integral part.

The Co^{60} inventory at the HIRDL facility increased substantially this year and included shipments of very high specific activity material. The use of the gamma facility at HIRDL also increased substantially.

Several dosimetry systems were improved and a new portable inexpensive thermoluminescent dosimeter was developed.

Additional data were obtained from comparisons of Co^{60} and Cs^{137} plaque source dose distributions in homogeneous and heterogeneous targets.

Additional computer codes were developed which readily handle cases involving a wide range of source and target geometries and materials.

Assistance to the AEC Food Program increased substantially; it included engineering modification and/or calibration of 12 irradiators.

In the exploratory research and development area the principles of the design and operation of radiation chemical reactors were investigated. During the past year, effort on isothermal reactors was broadened considerably. Work in the radiation treatment of liquids and particulate materials was increased and work was started in new areas of investigation that are concerned with problems of heat release in chemical reactors and problems of reactor control.

Most of the effort on direct conversion studies has been phased out because of budgetary limitations. A small chemical physics effort is continuing on the determination of metastable species.

Work is continuing on a method of computation to solve time-dependent transport problems.

A new program has been undertaken jointly with the Meteorology Group of the Instrumentation and Health Physics Department and the Analytical Group of the Hot Laboratory Division that will be

concerned with the feasibility of using naturally occurring differences in the ratios of the stable isotopes of sulfur as a means of studying sulfur compound pollution of the atmosphere.

Hot Laboratory Division

(05-05-03-00-0, 08-01-04-00-0)

The former isotope development and production efforts have been reorganized and reoriented with the development of medical applications of isotopes and fundamental nuclear and radiochemical research receiving new emphasis; almost all production has now been turned over to private industry.

In the area of isotope applications development, Te^{125m} is being prepared for a study of applications in transmission scanning, therapy via interstitial implantation, autoradiography, and labeled compounds. Uses of Tc^{99m} have been extended by procedures devised to incorporate it successfully into human serum albumin and calcium diethylene triamine pentaacetic acid. Studies with Tc^{99m} -labeled colloids have resulted in methods of altering the particle size by a factor of ten, permitting investigation of the effect of particle size on the colloid distribution within the reticuloendothelial system. Preparations were begun to make Fe^{52} for medical application studies. Prior to turning its production over to private industry, the Sr^{87m} generator systems originally developed at Brookhaven were further improved significantly.

Efforts in nuclear and radiochemistry have included a study of the chemical effects of Te isomer decay, in which evidence was found for at least three hot atom species in the decay of Te^{129m} by isomeric transition. A study of Szilard-Chalmers reactions induced in metallophthalocyanines by 14-MeV neutrons has provided additional evidence for our interpretation of differences in primary retention of activated atoms being due to differences in spin changes in going from the starting material to the product. A computer program that uses a single particle model incorporating realistic pairing corrections to calculate nuclide level densities is being written. Monte Carlo evaporation calculations were performed for all (α , n) reactions for which excitation functions are in the literature in an effort to correlate differences among targets. Excitation functions measured for ≤ 80 -MeV alpha-particle reactions on Al indicated that

much of the Na^{24} formed must be coming from something other than the $\text{Al}^{27}(\alpha, \text{Be}^7)\text{Na}^{24}$ reaction. Ternary fission is being studied by triple-coincidence counting equipment and by radiochemical search for Si^{32} and P^{32} in an old fuel plate. The pink and blue species of reduced Tc can be formed reproducibly, but thus far efforts to identify the oxidation state associated with each have been unsuccessful. A series of cross section measurements has been proposed to shed further light on cross section correlations that indicate that epithermal neutrons should be much better than thermal neutrons for making transplutonic nuclides.

In the area of analytical/physical chemistry research, several studies of mixed ligand complexes were performed. The Ni(II) chloride-bromide system in acetonitrile was found to be one of the rare cases in which mixed ligand complexes are formed to a lesser extent than would be expected from purely statistical considerations. A preliminary study of the equilibria involved in the aqueous iodide replacement of chloride in PtCl_6^{-2} indicates that a thermodynamic steric effect may exist. With the use of divalent copper in a systematic study of mixed β -diketone complexes in solvent extraction, it was shown that when two strong or two weak chelates are present the formation of a mixed ligand complex is what would be predicted from statistics, but when one of the ligands is strong and the other weak the stability of a mixed ligand complex is enhanced; in trivalent systems, studied with In, the same general trend was found, although, because of the larger valence, more combinations of ligands were possible and the systems were, therefore, more complex. Spectrophotometric and solvent extraction data provided evidence for the existence of a mixed metal complex containing In(III), Cr(III), and a hydroxycarboxylic acid. The electrochemical reduction of Tc was found to be a one-electron process in the absence of gelatin but a two-electron process when gelatin is present; the interpretation of this phenomenon is being considered. Computer simulation of hydrodynamic phenomena involved at the dropping mercury and rotating disc electrodes permitted theoretical treatment of a wide variety of electrochemical mechanisms. Computer generated time lapse displays of concentration vs distance profiles during electrolysis are proving valuable as a means of understanding the physical significance of what are often formidable mathematical problems.

Computer simulation was used to predict the variation of absorbance of orthotolidine with time in an evaluation of the oxidation kinetics of this compound; preliminary measurements agreed well with theory.

Metallurgy and Materials Science Division

**(04-40-02-02-1, 04-40-02-03-1, 04-40-02-05-1,
05-05-06-01-02)**

The program of the liquid metal center includes studies of (1) the 760° to 815°C corrosion behavior in sodium of materials for the liquid-metal fast-breeder reactor program, (2) the mechanism of corrosion of materials in liquid sodium, and (3) the chemistry of liquid sodium solutions.

About 23,000 hr of corrosion testing using thermal convection loops have been completed. Measured corrosion rates to date are low. Corrosion increases with Ni content of the alloy; both Ni and Cr are leached from the high-temperature specimens. Weight-change data indicate that Co-base alloys and type 316 stainless steel (SS) are comparable in their resistance to sodium corrosion. Cu in Na neither precipitates upon nor penetrates into type 304 SS in the high-temperature portion of a loop; Cu deposits were found adjacent to the valve leading to the cold trap. Development work on Co-base alloys indicates that alloys containing 2 to 3 wt % Ti have the most desirable properties.

Two forced-circulation Na loops have been completed. Heat generated in their test sections causes an inlet-to-outlet Na temperature rise of $\approx 50^\circ\text{C}$. Weight-change measurements for a short run indicate that corrosion rate is correlated with Na temperature, but that Mo is not corroded at temperatures up to 760°C.

More than 180 samples have been taken in attempts to determine the solubilities of Fe, Ni, and Cu in Na. Above 400°C, the Cu data agree well with results at both Atomics International and Los Alamos Scientific Laboratory. At lower temperatures, particulate Cu was believed to have caused erratic results; data from the second run, designed to minimize this problem, lie on a reasonable extrapolation of the high-temperature results. The Fe and Ni data scatter considerably, perhaps for the same reason; a number of analyses for radioactive Fe indicated none present, which suggests

that the solubility of Fe is less than the detection limit of 0.05 ppm. An apparatus for studying the corrosion kinetics is being assembled.

An apparatus has been built that uses the oxygen meter as a tool in studying the effects of both metallic and nonmetallic impurities on the activity of oxygen in Na. Ca and Li are very effective in reducing O activity at temperatures as low as 300°C. Uranium foil has been found to be a useful, removable getter for O in Na at 400°C; weight changes of the U can be used to calibrate the meter. An apparatus for studying C-Na interactions has been built, as well as a loop to provide well-characterized Na for chemistry studies. Convective mixing has masked any possible electromigration of O in Na. A revised apparatus has been built but not yet tested.

The blank in the amalgamation technique for determining O in Na can be related to the surface area of the glass in contact with the Na amalgam. Both the amalgamation and vacuum distillation methods give comparable results for Na samples containing ≈ 10 ppm O; however, the distillation method has a zero blank. The isotope dilution method for O in Na continues to be developed; O^{18} is added as Ag_2O^{18} . The critical step is the conversion of Na_2O to CO, since the resultant Na must be removed rapidly to prevent reaction reversal. The possibility of first converting Na_2O to an oxide of a nonvolatile metal, such as Mo, is being explored.

The high-temperature embrittlement effect has been investigated in several Fe, Co, and Ni-base alloys. All three types appear to be embrittled at 800°C after an exposure of 1.3×10^{20} nvt. The microstructure of stainless steel appears to affect its sensitivity to high-temperature embrittlement. Repeated deformation of type 304 SS at 77°K followed by reheating between 650° and 815°C breaks up the original austenite grains and renders the material more ductile both before and after irradiation. Material given the thermal treatment elongated 28% at 760°C after 1.3×10^{20} nvt, a value appreciably less than the 87% elongation in the unirradiated state.

The major effect of irradiation on pure iron is an increase in the athermal long-range internal stress, and not the stress at the rate-controlling barrier. Studies of the saturation of radiation damage to Fe and carbon steel indicate that, of the materials studied, damage in Ferrovac iron saturates at the lowest flux and damage in HY80

steel at the highest. Defect analysis suggests that more than one process is occurring.

Neutron irradiation appears to affect the rate-controlling slip process in Fe only when experimental conditions are designed to prevent moving dislocations from sweeping irradiation defects out of the lattice before deformation measurements can be made. Under these conditions, a neutron dose of 1.3×10^{20} nvt at $\approx 90^\circ\text{C}$ changes the rate-controlling slip mechanism to one based on tetragonal distortions which are created by radiation defects in the lattice, analogous to previously observed effects in Cu, although the defects in Fe are much smaller and more closely spaced.

When Fe specimens are deformed slightly at 77°K, the only apparent effect of neutron irradiation at 77°K was that the unirradiated specimens contained internal dislocation sources, while the irradiated specimens did not, as observed by electron transmission microscopy. Optical examination showed surface cracks on irradiated but not on unirradiated specimens. The internal dislocation sources are almost certainly due to precipitates of ϵ carbides in the Fe. Their precipitation, after some segregation, can be caused by high elastic stress or by irradiation to relatively low doses (1×10^{16} nvt at 60°C). They are decomposed by higher doses ($\approx 2 \times 10^{18}$ nvt at 60°C) because of gettering of the C by radiation defects.

When the Fe contained sufficient C to form Fe_3C , irradiation to 2×10^{20} nvt had no detectable effect on the microstructure of Fe-0.35% C, but appeared to reduce the concentration of finer particles of Fe_3C in Fe-0.03% C, which suggested partial decomposition of Fe_3C also.

Electrical properties of ThC-ThN solid solutions are similar to those of nonstoichiometric thorium carbides. Both ThB_4 and ThB_6 have metallic electrical properties with two conduction electrons per atom Th. Replacement of Th atoms with U in ThC increases the compound's electrical resistivity. Susceptibilities of nonstoichiometric ThC and the ThC-ThN systems have been measured and found to be determined primarily by the concentration of holes in a two-band model.

Characteristic temperatures for ThS, ThN, $ThC_{0.91}$, $ThP_{0.95}$, Th_3P_4 , ThO_2 , and ThB_6 were determined from measurements of x-ray diffraction peak intensities as a function of temperatures. The entropies of these compounds calculated from the data are in good agreement with the literature for the systems for which accurate data are known.

The K-graphite system has been found to be similar to the systems of graphite with Rb and Cs. The heats of reaction for all stages decrease in the order Cs, Rb, K, and, presumably, Na, which accounts for the low stability of Na-graphite compounds.

The maximum Cs compound between Cs and two types of carbon black was C_8Cs , as in the graphite Cs compounds. The nonhomogenous structure of the carbon blacks leads, however, to phase changes occurring over a range of pressures, and hysteresis in one instance. The threshold pressures for formation of alkali metal compounds were calculated; they increase in the order Cs, Rb, K, and Na, so that initiation of Na-graphite reaction requires pressures of the order of magnitude of the vapor pressure of Na.

A hard-sphere model for the structure of liquid metals has been used, with reasonable success, to calculate the self-diffusion coefficients and velocities of sound in liquid metals near the melting point. The calculations of the temperature dependences of the diffraction pattern and the velocity of sound have also been reasonably successful. The x-ray diffraction data for Na have been shown not to provide an unambiguous test of the Born approximation formula for electrical resistivity. The resistivities of liquid Hg-Au alloys decrease rapidly with Au concentration, as do Hg-Sn alloys with Sn, in contradiction to theoretical models for the effect; a decrease, although much smaller than that observed, can be calculated by conventional pseudopotential methods with use of a hard-sphere model.

The thermoelectric powers of dilute alloys of Ag, Cd, In, Sn, and Sb in Na have been measured and found to be linear functions of temperature in the range studied. The measured results agree quite well with calculations made with use of the Heine-Animalu pseudopotentials. Density measurements indicate little excess volume of mixing for Na and Sn, but appreciable contraction upon mixing Na and In.

A model for electromigration in liquid alloys has been developed which indicates that the alloy component having the greater resistivity, when pure, should be preferentially transported to the anode. Reformulation of previous data according to this model suggests that the migration rate constant increases linearly with temperature. Migration of Pb in Sb and Sb in Pb was studied. The results agree with the present model, but not with the relative mass criterion commonly discussed in

the literature. Further, a comparison of all reliable data in the literature with the present model shows a linear relationship between the amount of electromigration in an alloy and the difference in resistivity of the two components.

The electrical resistivities of the essentially two-dimensional alkali metal-graphite compounds have been measured; their temperature dependence is composed of several linear regions.

The thermodynamics of the superconducting-normal state transition have been formulated and used to interpret the hysteresis observed in superconductors. Pinning and critical state models are based on observations that retained fields in hysteretic superconductors exist in the form of gradients; these, in turn, are explained in terms of surface energies and activity coefficients. Magnetic induction is assumed to change the surface and interface energies of metals when they enter the superconducting state. Measurements have been made that demonstrate the validity of the assumptions.

Studies of superconducting phenomena at temperatures below 0.1°K have been initiated. Superconductive thin films of pure metal layers of Al, Sn, or In between dielectrics can have higher temperatures of transition than the bulk metals. However, in the very thinnest films, the critical temperature decreases as the film gets thinner. Measurements of superconducting properties of thin films deposited *in situ* are being made, as well as studies of the proximity effects between superconducting and magnetic layers, Knight-shift measurements in small particles, and high-field magnetoresistance in Bi.

Failures in brazed joints in magnet coil conductors at the AGS were shown to have resulted from incomplete melting of the brazing alloys. Failures in fatigue specimens of cermet fuel for the proposed pulsed reactor were shown to have originated in cermet areas of irregular UO_2 particle size and distribution. The electron beam micro-analyzer clearly indicated the structure of Nb-Nb₃SN superconducting tape and the errors associated with fabrication of the specimen examined.

Engineering Division

(04-40-03-01-1, 04-50-50-01-1, 04-50-60-10-01,
04-50-60-40-03)

The work of the Heat Transfer Research Group was primarily devoted to the study of forced-con-

vection heat transfer to liquid metals. It covered both single-phase and two-phase (boiling) flow, and included both analytical and experimental studies.

In the single-phase work, an analytical study was carried out for the case of laminar flow in thermal-entry regions in circular channels, where the velocity profile was fully developed and where axial conduction was taken into account. The results showed that, above a Peclet number of ≈ 50 , the effect of axial conduction on the local heat transfer coefficient was negligible. Also, in the single-phase work, an experimental project was carried out to measure the effect of rod displacement on the heat transfer behavior of mercury when flowing in-line through an unbaffled rod bundle. This project was relevant to the design of fuel element subassemblies and intermediate heat exchangers for sodium-cooled reactors. It was found that when a rod is moved off-center, its average heat transfer coefficient drops, as well as those of the rods toward which it moves. The coefficients of the rods from which it moved away increase, but the over-all average of all the rods decreases. This decrease can be appreciable.

In the boiling studies, emphasis centered on the phenomenon of incipient-boiling superheat in alkali metals, and a combined analytical-experimental study was carried out. The subject under investigation was the effect of prior temperature and pressure to which the heating-surface/liquid-metal system was exposed. Predictions based upon a refined analytical model were in good agreement with experimental results obtained with potassium. This information is pertinent to the operation of both sodium-cooled reactors and liquid-metal boilers in Rankine power systems.

In earlier experimental studies carried out at Brookhaven, it was observed that, because of the large difference between the liquid and vapor velocities in liquid metal boilers, the vapor temperature can be appreciably above the saturation temperature. Since over most of the boiler length there is considerable liquid entrained in the vapor in the form of fine droplets, an analytical study was undertaken to formulate quantitative relationships for estimating rate of evaporation of droplets, their transient thermal behavior, and their effects on the superheated vapor. During the past year, it was found that the evaporation process consists of two distinct time domains: one during which it is controlled by nonequilibrium vapor pressure difference, and a second during which it is controlled by

normal heat-transfer/mass-transfer with the superheated vapor.

In addition to the liquid-metal heat transfer work, a small effort was directed toward heat transfer problems arising in high-temperature, direct-conversion systems. Accordingly, an analytical study was carried out on transient heat transfer in MHD channel flow. The effects of step changes in pressure gradient, magnetic field, and wall temperature on heat transfer were determined. Some interesting results are given in graphical form in the body of this report. A second analytical study was carried out in which the influence of axial conduction on thermal-entry-region heat transfer in MHD channel flow was determined for a variety of operating conditions.

In the coming year, the research program will proceed along essentially the same lines, with increased emphasis on heat transfer with sodium. A new forced-convection loop is being constructed for experiments with sodium at temperatures up to 1600°F. The specific objective of this new project is to obtain data on the important problem of interfacial effects (solid-liquid interface roughness, microstructure, purity, etc.) on heat transfer under both liquid and boiling conditions.

As a part of the conversion of high-level radioactive wastes to stable solids, a process has been developed at Brookhaven for incorporating the fission products into phosphate glass. This process is one of three waste solidification processes selected for evaluation on a prototype scale in a demonstration program at Battelle Northwest Laboratories.

In support of the Battelle prototype, a pilot plant has been operated at Brookhaven with a variety of simulated Purex wastes, which reflect higher fuel burnup and advanced fuel reprocessing techniques. In view of the importance of platinum as a material of construction for melter crucibles an extensive study was carried out to measure the effects, on the strength of the metal, of high temperature and of migration of waste component elements into the platinum. The study was completed and no serious deleterious effects were found. In the interest of obtaining high stability of the glass product, sulfuric acid, when present as in Purex 2, is volatilized in the glass-forming step. Studies are being carried out on the decontamination of the high sulfate condensate by means of distillation and fractionation.

Efforts were continued during the year on the investigation of a process for dispersing high-level

wastes from fluidized-bed volatility fuel reprocessing in glass matrices. Emphasis was placed on providing design information for a waste processing facility for the fluidized bed volatility pilot plant at Oak Ridge National Laboratory. In this connection several pieces of small-scale equipment were designed, constructed, and operated.

A system is under development for removing Kr and Xe from nuclear fuel reprocessing off-gases. The low concentration (about 100 ppm) of these chemically inert materials in the process stream makes it necessary to resort to operation under cryogenic conditions to achieve an effective separation. The problem is complicated by radiolytic generation of ozone within the system.

During the past year, the research carried out in the Fission Product Release Program primarily dealt with problems related to the safety of sodium-cooled fast reactors. In addition, some effort was also expended to complete work related to the safety of water-cooled reactors.

Both analytical and experimental studies are under way to investigate the behavior of fission products of Cs, Rb, Sr, NaI, Ba, Te, and Sb in sodium. Recently, thermodynamics measurements of the NaI-Na system were completed. The experimental results were found to be in excellent agreement with predictions based on the phase diagram and those based on the average potential model of solutions. Experimental Cs-Na vaporization results were found to be in good agreement with analytical predictions.

A study is also under way to identify the parameters controlling fission product release from condensed phases into a flowing gas stream. Experimental results on the release of iodine from molten U was explained in terms of liquid phase diffusion with an interfacial resistance term. The release of Cs from Na was found to depend primarily on liquid phase diffusion, although a small gas phase resistance was observed experimentally.

Another phase of the program deals with the formation, transport, and agglomeration of radioactive aerosols emanating from nuclear materials. Studies of UO_2 , PuO_2 , $\text{UO}_2\text{-PuO}_2$, and fuel oxide-sodium aerosols were carried out during the past year. The individual oxide aerosols were found to coagulate over long periods of time with a rate constant of $\approx 10^{-8} \text{ cm}^3/\text{sec}$. However, the presence of a sodium aerosol was observed to reduce the coagulation time of the oxide particles.

Experiments were also done to investigate the radiation decomposition of CH_3I , a species formed during the release of iodine from UO_2 into steam-air mixtures. A reaction mechanism and a related analytical equation were deduced that satisfactorily explain the decomposition for three limiting concentration regions.

The Engineering Assistance Group contributed approximately 60,000 hr to the support of departmental programs during the year. The majority of this support was in the design and construction of experimental facilities used for research in radiation processing, liquid-metal heat transfer, experimental physics, materials for containing liquid metals, and advanced reactor concepts. The group also contributed to various national technical committees and the *High-Temperature Liquid-Metal Technology Review*.

The pulsed research reactor studies have concentrated on two general areas of work. Design techniques have been developed and applied to the areas of stress, thermal, and physics analysis, and experimental programs are in progress on fuel development, a critical facility, and pulsed neutron time-of-flight measurements. The studies are being carried out for two reference fast reactor systems – a pulsed reactor and an accelerator-injected pulsed reactor.

A 3-dimensional transient heat transfer code has been used to calculate the temperature distribution of the core hot pin as a function of time starting from uniform initial temperature to the equilibrium temperature cycling condition after many pulses. The code was modified to provide input information directly for another code that is being used to calculate the thermal stress distribution in the fuel pin. The thermal and stress analysis was performed for a typical pulsed reactor core fueled with a 60 vol % $\text{UO}_2\text{-Mo}$ cermet integrally clad with 0.015 in. of molybdenum. The calculations were repeated for the same fuel with Inconel cladding and there were some advantages over the molybdenum cladding.

In support of the critical experiment, survey physics analyses were made of cores with various compositions and geometries. Most of the analytical physics effort was directed toward the determination of the reactivity of the system as a function of the position of the reflector block that is used for reactivity pulsing. Various techniques for improving the characteristics of the reactivity pulse and for reducing the prompt neutron lifetime in the

core are being investigated in order to minimize the width of the power burst produced by the reactor.

A survey of candidate fuel materials for both the pulsed reactor and the accelerator-injected pulsed reactor has been completed. Several alloy and cermet fuel systems were selected for fatigue testing in the unirradiated condition and specimens of these have been manufactured. Two ultrasonic fatigue tests have been conducted on 60 vol % UO_2 -Mo cermet samples and the fractured specimens were examined metallographically. Both ultrasonic

fatigue tests at 14.2 kcps and mechanical fatigue tests at 80 cps are planned. Tensile tests are also being performed on fuel systems on which no tensile data are available.

A fast reactor critical assembly has been designed for experiments in support of the design studies. The first core to be assembled will have a critical mass of about 150 kg U^{235} , and Al in reduced density form will be used to simulate sodium.

Pulsed neutron time-of-flight measurements are being made in order to provide data for the optimization of the beam and beam source.

NUCLEAR ENGINEERING DEPARTMENT

BROOKHAVEN NATIONAL LABORATORY

ORGANIZATION CHART
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Reactor Physics Division

J. CHERNICK, H. KOUTS

Reactor Physics Theoretical Group

REACTOR SAFETY

Response of External Detectors to Power Tilts

At the request of the Division of Reactor Licensing, the response of external flux detectors to power tilts in a pressurized water reactor (PWR) core is being investigated. Changes in power shape may be associated with a number of mechanisms, including xenon transients, control rod motion, macroscopic core property changes, etc.

The sensitivity of the detector system to arbitrary power shapes can be determined most conveniently in terms of the adjoint or importance function for the reactor. The importance function has been mapped out for one-dimensional radial power tilts by means of diffusion theory calculations for a PWR. Additional calculations are being prepared to study azimuthal and axial power tilts as well as to find the effects of transport corrections.

M. LEVINE, A. ARONSON

Moderator Coefficient

In cooperation with the Division of Reactor Licensing, calculations were carried out for the Connecticut Yankee reactor to find the reactivity effect of coolant loss when the coolant contains dissolved boron. Discrepancies between BNL results and those quoted by the manufacturer were found. These appear to be due to the particular method used to calculate the thermal neutron spectra.

M. LEVINE, A. ARONSON

Plenum Reactor

The Na temperature coefficient of a liquid metal fast breeder reactor (LMFBR) can be shifted toward more negative values by enhancing the neutron leakage. This has been accomplished in various proposed reactor systems by core flattening and by modular core design. Another promising method that is being examined here is the introduction of regions of high sodium volume fraction ("plenum" regions) in the core. These

regions not only make the Na temperature coefficient more negative but also ensure that the reactor becomes subcritical on loss of Na.

The reactor considered here has core and blanket compositions typical of oxide-fueled LMFBR's, with a 4000-liter core volume. Two plenum regions, 1 ft thick, divide the core axially into three equal parts ≈ 20 in. high and 6 ft in diam. Both one- and two-dimensional multigroup diffusion calculations were made using a set of 22 group cross sections prepared by Argonne National Laboratory for large fast oxide LMFBR's. The over-all temperature coefficient of the reactor is small and negative as a result of introducing the plenum regions. However, the two-dimensional calculations show that there are subregions in both the core and plenum zones where the local Na temperature is still positive.

This local Na coefficient was mapped out through the use of two-dimensional multigroup diffusion and first-order perturbation calculations with the

Figure 1. Local sodium coefficient in a plenum reactor.

CRAM code. Figure 1 is a contour plot of lines of equal Na coefficient, in equal steps. The coefficient is positive in the shaded regions, i.e., reactivity increases with decreasing Na density in these regions. The time behavior of the reactor must be studied carefully for its behavior under perturbations, since reactivity changes are associated with the motion of heated Na between regions of differing temperature coefficient. Hence the dynamical stability must be treated with both space and time dependence.

For this purpose the power density and reactivity distributions were fitted with polynomials in r and z for use in numerical calculations. The time behavior is being examined for small perturbations where the power shape does not change appreciably, and preparations are being made for studying large perturbations where significant power tilts can occur.

M. LEVINE, G. LELLOUCHE,
A. ARONSON, W. BORNSTEIN

FAST REACTOR CRITICALS

Fast reactor spectra have been calculated for comparison with a number of British measurements in the VERA series. Various cross-section sets have been used for this work. The comparisons are being analyzed for information on cross-section inadequacies.

Data from Los Alamos experiments on simple reflected spheres of reactor-grade plutonium are being used to test cross sections obtained from the ENDF/B file. The ETOE system has proved satisfactory for this purpose and some bugs in the use of the MC² code have been eliminated.

J. CHERNICK, M. LEVINE, A. ARONSON, P. TU

FAST NEUTRON TRANSPORT

An analysis of space-dependent spectra in large blocks of nonmultiplying material can be used to obtain cross-section information of value for fast reactor analysis. For this purpose, studies have been made on neutron penetration in iron by means of a specially developed S_N code. In the neighborhood of prominent iron resonances, both flux peaking and flux depression can occur depending on the position of the detector and the size of the block. These effects are being analyzed for information on scattering anisotropy and resonance shape. The importance of the use of fine group structure near resonances has been demonstrated.

J. WAGSCHAL, M. LEVINE, J. CHERNICK

FAST REACTOR CODES

Codes for use of ENDF/B data have been converted for use on the CDC 6600 computer. The MC², DAMMET, ETOE package for producing multigroup cross sections is in the final stages of debugging and checking.

A. ARONSON

REACTOR DYNAMICS

Code Construction

The code system NOMURK is nearly complete. Still in the programming stage is a two-space dimensional form of the static shape section and a multitemperature space independent code for initial survey studies. Adjunct codes to reduce power and reactivity coefficient distributions from auxiliary multigroup codes to analytical form (by the least-squares method) are also nearly complete; this approach simplifies the input to NOMURK.

Xenon Dynamics

A wider region of asymptotic stability in the large was found for the space independent xenon-temperature problem. A complete mapping of the stability of the first harmonic (orthogonal to the fundamental) of a bare reactor controlled by xenon and flux feedback for a wide range of reactor sizes and flux coefficients was completed.

Flowing Coolant Dynamics

The effect of using a partial differential equation to characterize a flowing coolant and its temperature has been extensively studied to determine any effects on the stability boundary of various reactor models. The explicit power and reactivity spatial distributions were found to be quite significant in determining the location of the stability boundary.

Heat Exchanger Dynamics

An analysis of various mathematical models of heat exchangers and their effect on the location of the stability boundary was started. It has been noticed that the natural attenuation characteristics of a well designed heat exchanger damp out any small variations in core exit temperature on a single pass, and that the location of the critical stability boundary is not significantly affected by the presence of a heat exchanger.

G. LELLOUCHE

RELATION BETWEEN PULSED NEUTRON AND NEUTRON WAVE EXPERIMENTS

Two techniques that are used to investigate the properties of moderators are the pulsed neutron experiment and the neutron wave experiment. Both of these experiments are usually described by a perturbation series. In the pulsed experiment the decay constant and the fundamental flux eigenfunction are expressed as a power series in the buckling; in the wave experiment, the wave number (sometimes called the "complex inverse relaxation length") and the flux eigenfunction are expressed as a series in the excitation frequency. The relationship between the description of the two experiments was investigated, and it was shown that the perturbation terms, for both the eigenvalue and the flux, of one experiment could be expressed as a linear combination of the terms describing the other experiment. It was thus concluded that calculational techniques developed for one method could be used for the other with only trivial modifications, and that both experiments yield the same physical information about the moderator.

The general results are applicable to multiplying systems as well as to moderators and fast systems.

P. MICHAEL, M. MOORE

NEUTRON THERMALIZATION - DECAY CONSTANTS IN SMALL WATER SYSTEMS

The two-pronged analysis of pulsed neutron physics phenomena in the thermal region has been completed. The theoretical studies of pulsed neutron experiment time decay constants in small systems with isotropic degenerate scattering kernels was extended to give approximate expressions for the fundamental mode eigenfunctions or distribution functions in slab geometry (i.e., the energy, angle, and spatial dependent asymptotic flux). Leakage angular distributions and energy spectra were determined.

The extensive computations of fundamental mode decay constants for spherical light water systems using realistic H₂O scattering models (Nelkin model and Young and Koppel's anisotropic model) were also brought to a conclusion. The energy, angular, and spatial dependence of the asymptotic flux was computed numerically as were the leakage angular distributions and energy spectra. The separability of the asymptotic flux into its dependencies upon the independent variables was ex-

amined. It was found that the flux was definitely not separable in small systems and that the energy spectrum and angular distribution of the flux varied considerably with position.

The effect of scattering anisotropy upon the calculation of the decay constant was investigated by including various orders of anisotropy in the scattering kernels. The results showed that the inclusion of only *P*-1 scattering yielded excellent results (in agreement with calculations using higher order scattering and experiment) for both decay constant and flux even in very small systems while *P*-0 scattering calculations led to very poor results. However, the use of "transport corrected" cross sections in conjunction with isotropic scattering led to good results with acceptable accuracy (when compared with both experiment and higher order calculations). The effect of chemical binding was examined by using a gas model that treated the hydrogen atoms as free atoms. This model not only led to energy spectra that were in poor agreement with those computed using the more realistic kernels but resulted in decay constants that were as much as 50% above both the realistic model calculations and experiment.

J. DORNING

ITERATION METHODS

Intermediate Resonance Absorption

The intermediate resonance (IR) formulation of the problem of resonance absorption has proved useful in giving analytic formulae from which one may calculate resonance integrals for the fissile nuclides. Two improvements to the IR formulae have recently been made. In one, a different iteration procedure is used that yields a more rapidly convergent result and better numerical values. In the other, the IR formulae are modified to a single equation for one fundamental quantity, instead of a coupled set of equations for the individual IR parameters. This is particularly useful for systems with many scattering species.

Iterative Solutions by Means of Trial Operators

The problem of finding a weighted average of an unknown solution to an inhomogeneous equation has been examined. An analytical approximation technique was developed in terms of an iterative series involving a trial operator. By choosing the operator so that successive terms in the series vanish, one obtains a solution that has characteristics similar to variational solutions to the prob-

lem. By calculating the next term in the iterative series, the trial operator approach has the added features of giving error estimates, the sign of the error, a testing ground for the quality of classes of trial operators or functions, and a possible means of determining upper and lower bounds to the exact result. By means of several examples in reactor physics it has been shown that this method can give useful analytical approximations, with results that may be superior to variational calculations.

R. GOLDSTEIN

REACTOR KINETICS

Perturbation Expansion

A generalized perturbation approach to nonlinear space-independent kinetics problems has been developed. It extends previous work on oscillatory problems to parameter regions with all real linear roots. The results (Figure 2) permit determination of realistic bounds on perturbations in regions where the system may be linearly stable and nonlinearly unstable (i.e., finite escape time). One major advantage of the method is that it is straightforward and requires no special insight or

experience, as do topological and Liapunov-function techniques. It is especially applicable to safety studies on the simple models used for fast-reactor excursions where space-dependent effects may be ignored as a first approximation.

This perturbation approach was extended to space-dependent problems by considering the nonlinear coupling between the fundamental and first harmonic spatial modes in the xenon problem. It was found that, for certain spatial forms of the initial disturbance, inclusion of the effects of the first harmonic can have a pronounced destabilizing influence on the fundamental spatial mode.

Excursion Models

A critical review of reactor excursion models was completed. Comparison with experiment showed that the Fuchs-Nordheim model is not as good as a two-term expansion introduced by Corben. Also, a linear energy approximation to the feedback is not as good as a nonlinear one. This raises questions concerning the calculation of the Doppler effect in terminating excursions in fast reactors.

L. SHOTKIN

Zero-Power Describing Functions

An approximate zero-power describing function has been derived that is valid for all excitation frequencies. It avoids the singularity at low frequency that was characteristic of all previous zero-power describing functions. This was accomplished by using an expansion in modified Bessel functions rather than the customary algebraic polynomial expansion.

L. SHOTKIN, A. AKÇASU

FLUID DYNAMICS

Two-Phase Flow

A critical rederivation of the conservation laws for two-phase flow has been started. Particular attention is being focused on the concept of averaging over a channel cross section and on the problems associated with thermodynamic equilibrium. Both of these effects are important in the flow of liquid metals in fast reactors. It seems, for the most part, that the same equations and mathematical techniques used for boiling water flow can be used for boiling metal flow. The major differences are the inclusion of heat conduction in the fluid and the use of suitable correlations for the slip ratio and degree of superheat. Reliable correlations of this sort appear, at present, to be lacking.

L. SHOTKIN

Figure 2. Bounds on permissible disturbances from equilibrium; a comparison of various analyses of a simple kinetics model.

Figure 3. Development of the region of separation behind an accelerating sphere. These computer-drawn figures are contours of constant stream function as seen in a frame of reference moving with the sphere. The Grashoff number ($a_0 r_0^3 / \nu$) is 100; the sphere has a density eight times that of the fluid. The numbers at the lower right of each frame denote the distance the sphere has traveled from rest (measured in sphere radii). The Reynolds number ($\nu r_0 / \nu$) varies from 35 (upper left) to 39 (lower right). One can see how the eddy behind the sphere increases in length and becomes deeper.

Figure 4. Approach to terminal velocity of a sphere in a viscous fluid. The Reynolds number is divided by the square root of the Grashoff number for scaling purposes and plotted as a function of distance traveled from rest (in units of sphere radii); the two numbers associated with each curve are the Grashoff number and the fluid-to-sphere density ratio.

Solution of the Navier-Stokes Equation

Development of difference approximation methods in order to use digital computers to solve the Navier-Stokes equations for incompressible viscous fluid flow problems has been carried out. Improvements in the speed and capacity of computers are making it possible to solve problems that could not be handled by analytical techniques. The current work is aimed at the development of techniques and the determination of the range of validity, accuracy, and efficiency of various methods.

The particular method being studied uses the time-dependent Navier-Stokes equation written in terms of the stream function and the vorticity; central differences are used for the spatial part of the equations; the time derivative is handled by a fully implicit iterative technique. These choices were made in order to have difference equations that are correct to second order and that are numerically stable. The type of physical problem being considered is the motion of a body in an unbounded fluid; this requires that a relatively fine mesh be used near the body and that a large region in space be considered. Therefore, in order to keep the number of space points from becoming excessive, an irregular mesh is used, the size of the mesh increasing as one gets further from the body.

The method has been applied to the calculation of the motion of a sphere in a viscous fluid being acted upon by a constant external force (i.e., gravity) and being retarded by drag forces. A pair of dimensionless constants characterize the motion: one is the ratio of densities of the fluid and the sphere, the other is akin to the Grashoff number that is used in the description of convection. This latter parameter is essentially the ratio of the accelerating force to the viscous force, and in this work is defined as $a_0 r_0^3 / \nu$, where a_0 is the acceleration that the sphere would have in the absence of drag forces, r_0 is the sphere radius, and ν is the kinematic viscosity. Some representative results are shown in Figures 3 and 4. P. MICHAEL

Reactor Physics Analysis Group

FURTHER DEVELOPMENT OF THE HAMMER CODE

The HAMMER code is the principal tool used at BNL for the calculation of the spectrum, reaction

rates, and criticality of reactor lattices. It combines in a relatively consistent way a number of earlier codes and methods, but it still displays some serious misrepresentations of the physical processes and cross sections. As the use of the code continues, some of these anomalies have become apparent and a substantial amount of work has been invested in correcting them.

The overestimate of resonance capture inherent in HAMMER is probably the most serious error. Some improvement was made by introducing an exponential relation between the resonance integral and capture rate; the remaining errors, due to the use of two-region collision theory, the effect of cladding, and neglect of resonance overlap, have been removed by allowing an arbitrary reduction of the resonance integrals to match Monte Carlo reaction rates.

The flux mismatch between the thermal and epithermal parts of the neutron spectrum has been largely corrected by altering the slowing-down equations to take account of epithermal chemical binding and finite scatterer temperature. Various improvements of the edits have also been made and a routine has been developed to provide space-energy pictures (see Figure 5) of the neutron spectrum. Work has started on adapting the ENDF/B cross section library for use in the HAMMER code and it is expected that, with the various alterations made to the code during the past year, it will provide an adequate means of testing the ENDF/B data against integral experiments. H. CONNELL,

H. MIZUTA, B. SEHGAL

ANALYSIS OF BNL U²³⁵-GRAPHITE CRITICAL EXPERIMENTS

The graphite-moderated critical experiments with 93% enriched uranium-aluminum fuel plates were designed as "clean," almost homogeneous, bare cores. In four of these assemblies the fuel was 0.15 in. thick and the C/U²³⁵ ratio varied from 5700 to 23,000; the absorption spectrum was thus primarily thermal. Critical bucklings and spectral indices were measured, and experimentally determined corrections were made for neutron reflection and control rod channels.

The analysis of these assemblies is extremely sensitive to the leakage calculation, since about half of the neutrons leak out. Two methods were used for estimating the leakage and the lattice reactivities. In the first, the conventional B_1 approxi-

mation was used in which the first two spatial moments are correct and good estimates are made of the higher moments. This method is incorporated in the HAMMER code, which also provides the lattice reactivity. In the second, the leakage was calculated by the moments method and was combined with the HAMMER zero-buckling calculation to give the lattice reactivity.

The Monte Carlo code MOCA-2A was used to calculate the first three even moments of the slowing-down distribution. The moments expansion does not converge rapidly and the higher moments could be estimated only by fitting the initial MOCA moments to the moment sequence of a combination of age, diffusion, and single collision kernels. In both methods the thermal leakage was calculated in the B_1 approximation, since a Monte Carlo code with upscattering was not available.

The thermal absorption cross section and the epithermal scattering cross sections for graphite were chosen to reproduce the measured L^2 and τ . In the thermal range the GASKET-FLANGE kernel was used for graphite and the epithermal scattering parameters include the effect of chemical binding. The U^{235} epithermal cross sections conform

to the evaluation of BNL 325 and the recommendations of Feiner.

The values of k_{eff} obtained by both methods lie within 0.3% of unity, so it appears that the B_1 approximation describes the leakage quite accurately, even for such high leakage systems. The calculated results for cadmium and activation ratios for Mn^{55} , Pu^{239} , U^{235} , Au^{197} , and In^{115} foils fell largely within the stated uncertainties of the measurements.

B. SEHGAL

THE BRITISH BICEP LATTICE EXPERIMENTS

Some of the problems encountered in the analysis of the British graphite exponential experiments were mentioned in the last annual report; since then, this work has been finished. In brief, the calculations showed that the cross sections and theory that have been found satisfactory for water reactors also yield fairly good agreement with the measured bucklings in natural, depleted, and slightly enriched uranium-fueled graphite lattices. For the twelve lattices studied the average eigenvalue for the measured bucklings was 0.9969 ± 0.0043 .

Figure 5. Typical HAMMER cell neutron spectrum in a natural uranium-fueled BICEP lattice. Horizontal axis: lethargy; vertical axis: flux per unit lethargy; other axis: distance from center of cell in cm.

Since the leakage was highly anisotropic in these assemblies, the moments method was chosen, the Monte Carlo MOCA-2A code generating the migration moments. The computed second moment anisotropies agreed very well with Benoist's one-group theory, but the anisotropy in the higher moments was also important and this is not usually accounted for. The resonance capture in U^{238} was calculated by Monte Carlo methods in the resolved range and the infinite multiplication factor was then computed using the Monte Carlo corrections in the HAMMER code.

The experimental errors due to graphite cross section, hydrogen content, and buckling uncertainty were comparable to the Monte Carlo leakage and resonance capture uncertainties. The net effect is to assign errors of 0.5% or larger to all the eigenvalues and this limits the usefulness of the BICEP experiments in verifying theoretical methods and cross sections. It can be said, however, that no basis has been found for the British contention that the resonance integral of U^{238} is grossly overestimated when computed from cross sections consistent with Hellstrand's experiments.

R. HELLENS

ANALYSIS OF BROOKHAVEN U^{233} - ThO_2 LATTICES

The exponential experiments performed at BNL with 3% U^{233} -enriched ThO_2 fuel rods in light and heavy water comprise the only systematic set of integral data that can be used to check the cross sections of both U^{233} and Th^{232} . A broad range of reactor spectra was provided in these experiments by changing the pitch so that the fraction of fissions above 0.625 eV varied from 0.04 to 0.6. The core leakage was varied from -4 to 36% of the neutrons by boron poisoning of the light water moderator.

In the analysis of these experiments the thermal ($0 \leq E \leq 0.625$ eV) cross sections for U^{233} and Th^{232} were taken from the ENDF/B evaluation. The epithermal fission and capture cross sections of U^{233} were taken from BNL 325 with the proviso that the total fission and capture integrals conform to Feiner's recommendations. The epithermal capture cross sections of Th^{232} were constructed to yield the measured resonance integrals.

The calculations were done with the HAMMER code except that the resonance absorption in the energy band between 17.6 and 1234 eV is calculated by the Monte Carlo code REPETITIOUS. The

resultant eigenvalues for the light water-moderated lattices display a systematic tendency to decrease with increasing boron concentration or decreasing buckling. The obvious explanations are that either the calculated thermal disadvantage factor, ξ_{Dy} , is too high or the calculated age is too short. The calculated disadvantage factors are indeed $\cong 2\%$ higher than those of the measurements; however, this discrepancy may be due to the flux peaking and dipping in the measuring Dy foils. The possibility of calculated age being too short is confirmed by a comparison with the Roberts-Pettus experiment of ThO_2 rods in mixtures of light and heavy water. An increase in the calculated age by $\cong 2\%$ removes most of the trend with buckling and brings the values of k_{eff} for light water lattices to within 0.8% of unity. The calculated values of ρ_c^{02} , the ratio of epicadmium to subcadmium captures in Th^{232} , agree with the measurements within the estimated errors.

The calculated eigenvalues for the D_2O -moderated lattices are on the average too low by $\cong 1.2\%$. This discrepancy is not yet understood. These lattices are constructed to approximate bare core geometry and $\approx 35\%$ of the neutrons leak out of the core. A systematic overestimate of the measured buckling by $\cong 0.5 \text{ m}^{-2}$ can account for the discrepancy in reactivity between calculations and measurements. The calculated ξ_{Dy} are again $\cong 2\%$ higher than those of the measurements and the ρ_c^{02} values are largely in agreement. The calculated values of δ_{23}^{02} , the ratio of fissions in Th^{232} to those in U^{233} , are lower than those measured, but not by enough to explain the reactivity discrepancy.

The general agreement of theory with measurements of the U^{233} -Th lattices is not as good as that found with slightly enriched uranium. It is possible that systematic errors exist in the buckling measurements for the D_2O -moderated lattices and that some appreciable cross-section errors remain to be found.

B. SEHGAL

SPECTRUM-SHIFT LATTICE EXPERIMENTS

The critical experiments performed at Babcock & Wilcox with two enrichments of fuel, two cladding materials, and mixtures of light and heavy water provide an unusually extensive range of neutron spectra for buckling and cell parameter measurements. Earlier analyses of these experiments have not been very successful, since about three-quarters of the captures and fissions occur

epithermally in the tight lattices and extreme precision is consequently needed in computing the epithermal effects. This series of measurements has been found very useful for testing the HAMMER code with Monte Carlo methods.

If only those lattices with $<15\%$ leakage are considered, the eigenvalues obtained from measured bucklings show a consistent increase with the amount of epithermal capture and fission after the reaction rates have been adjusted to agree with Monte Carlo results. The U^{235} resonance line shape used in the HAMMER library yields an epithermal value of α that decreases from the infinite dilution value by as much as 20% with shielding. From comparisons between Al- and steel-clad fuel it appears that the measurements could be best explained by a substantially smaller α variation and by the use of resonance integrals for the steel constituents that are consistent with integral values of ≈ 2.5 b, rather than with the differential cross section value of 1.4 b. The unusually close packing of the eigenvalues from these low buckling experiments and their marked sensitivity to the accurate calculation of epithermal events suggest that they will be particularly valuable for the checking of lattice design codes and the ENDF/B data file. The eigenvalues calculated for more leaky lattices are quite randomly distributed over $\approx 3\%$ in reactivity and they should probably be rejected.

R. HELLENS, H. MIZUTA

SMALL REFLECTED ASSEMBLIES

Since much of our experimental data for both fast and thermal reactors is obtained from small reflected assemblies, a study of the theory of such assemblies has been undertaken. The theory commonly used for thermal reactors is known to be substantially incorrect and similar errors are suspected in fast reactor calculations. The principal tool for this work is ANISN, a one-dimensional multi-group DSN code with the important capability of including anisotropic scattering. Much effort has been expended to make ANISN operable on the CDC 6600 and to prepare the necessary cross-section libraries for both fast and thermal spectrum calculations. An exact description of an axial exponential flux dependence has also been incorporated in the code to eliminate the need for a mixed diffusion theory- S_n treatment of exponential experiments.

Calculation of bare one-group assemblies with an axial exponential shape by diffusion theory, the

B_0 approximation, DS4, and DS8, have demonstrated that the B_0 and DSN eigenvalues agree, as they should, when the assembly is sufficiently large to generate a pure mode in the interior. Near the center of the large assemblies, however, deviations from a J_0 shape become more noticeable as the order of the DSN calculation decreases. Thus it can be expected that low-order DSN calculations may give spurious indications of a departure from the asymptotic core spectrum. A similar study of two-group reflected cores showed that the errors in DS4 calculations for typical exponential assemblies are comparable, but of opposite sign, to those of diffusion theory. In this situation B_0 theory is not applicable, but it could provide the rationale for corrections to diffusion theory.

In order to study the neutron spectrum transients between core and reflector, a few calculations in DS4 have been performed with 54 slowing-down groups and 5 thermal groups. Few-group calculations using the same cross sections then provided a comparison with conventional methods. Several points emerge from this work. Few-group calculations with one or five thermal groups show that the improved thermal spectrum description increases the eigenvalue of a small (12-cm radius) core slightly (0.3%) while that of a large (25-cm radius) core is unchanged. Similarly, the 59-group DS4 eigenvalue for the large core is essentially the same as that from four-group diffusion theory, but for the small core it is 1.5% higher. This is very similar to the trend observed from analysis of experiment, and it indicates that the accurate description of fast flux transients is vital for the analysis of small assemblies. However, there is reason to believe that the DS4 calculations are overestimating the correction to diffusion theory by a substantial margin. Because of computer limitations, it is difficult to improve the accuracy of the transport theory calculations in the angular mesh without sacrificing some detail in space or energy. The effect of such adjustment of the three-dimensional mesh is being explored.

H. LUDEWIG, R. HELLENS

Reactor Physics Experimental Group

URANIUM-GRAPHITE CRITICAL ASSEMBLIES

All data-reduction has been completed for the program of measurements made with nearly homogeneous critical assemblies of highly enriched uranium in graphite.

The compositions and dimensions of the assemblies are given in Table 1. Table 2 lists the critical bucklings (B^2), effective multiplication constants (k_{eff}), and disadvantage factors (D , defined as the ratio of the average fission-inducing flux in the moderator to that in the fuel). The values in the tables have been corrected (where needed) for control-rod perturbations and room return effects.

The temperature coefficients, $d\rho/dT$, and the ratio of the prompt-neutron generation time to the delayed-neutron fraction, l/β , are given in Table 3. An investigation of the observed prompt-neutron decay as a function of detector location in the assembly with $C/U^{235} = 958$ showed that the measurements of l/β were not affected by the presence of higher harmonics. Since in the other assemblies the higher harmonics decay even more rapidly relative to the fundamental, the same conclusion also applies to these.

The infinite-dilution Cd ratios and the infinite dilution activation ratios of a number of detectors relative to Mn are given in Table 4 for the three assemblies in which they were measured. The activation ratio, A^* , of a pair of detectors, x and y , is defined as

$$A^* = [A^{(x)}/A_r^{(x)}]/[A^{(y)}/A_r^{(y)}]$$

where $A^{(x)}$ and $A^{(y)}$ are the activities of detectors of type x and y in the unknown system, and $A_r^{(x)}$ and $A_r^{(y)}$ are the activities of the detectors in a reference spectrum. The reference spectrum was that of a graphite thermal column at room temperature. The effective cutoff energies, E_c , of the Cd covers (thickness = 0.045 in.) used to obtain the Cd ratios are also given in the table.

J. PHELPS,
E. WEINSTOCK

CALIFORNIUM EXPERIMENT

A preliminary attempt was made to measure the rate at which Cf^{254} is produced by successive capture of two epithermal neutrons in Cf^{252} . A 0.01- μg sample of Cf^{252} was exposed in the V-15 in-pile irradiation facility of the Brookhaven High Flux Beam Reactor (HFBR) for 6 days. After the sample was removed, it was counted with BF_3 detectors imbedded in paraffin in order to detect the neutrons from spontaneous fission of Cf^{252} and Cf^{254} . Computations based on predicted cross sections and resonance integrals for fission and capture [A. PRINCE, Thermal neutron cross sections and resonance integrals for transuranium isotopes, *Trans. Am. Nucl. Soc.* **10**, 228 (1967)] indicated that an increase of $\approx 30\%$ in the spontaneous fission

Table 1

Composition of Uranium-Graphite Assemblies

C/ U^{235} atom ratio	Dimensions, cm	Atomic densities, atoms/cm ³			
		C ($\times 10^{22}$)	U^{235} ($\times 10^{18}$)	U^{238} ($\times 10^{17}$)	Al ($\times 10^{20}$)
22900	$162.45 \times 183.36 \times 182.88$	8.518	3.720	2.702	2.141
17180	$139.67 \times 168.31 \times 182.88$	8.501	4.948	3.593	2.847
11450	$133.19 \times 132.95 \times 182.88$	8.486	7.412	5.382	4.265
5724	$109.06 \times 121.13 \times 182.88$	8.425	14.72	10.69	8.469
958	$98.27 \times 101.71 \times 182.88$	8.121	84.75	48.81	29.34

Table 2

Critical Parameters of Assemblies

C/ U^{235} atom ratio	Critical buckling, B^2 ($\times 10^{-4} \text{ cm}^{-2}$)	Multiplication constant, k_{eff} (at 20°C)	Disadvantage factor, D
22900	9.33 ± 0.02	1.0058 ± 0.0011	1.063 ± 0.006
17180	11.02 ± 0.03	1.0027 ± 0.0011	1.054 ± 0.007
11450	13.46 ± 0.05	1.0033 ± 0.0012	1.049 ± 0.007
5724	16.88 ± 0.08	0.9988 ± 0.0020	1.029 ± 0.006
958	20.93 ± 0.12	0.9935 ± 0.0036	1.076 ± 0.009

Table 3
Temperature Coefficients and l/β

C/U ²³⁵ atom ratio	$dp/dT, \phi/^\circ\text{C}$	$l/\beta, \text{msec}$
22900	-4.43 ± 0.07	173 ± 3
17180	-4.0 ± 0.4	143 ± 3
11450	-2.7 ± 0.5	99 ± 2
5724	-1.69 ± 0.24	54 ± 1
958	-0.45 ± 0.02	9.92 ± 0.09

Table 4
Infinite Dilution Cadmium and Activation Ratios

Detector	E_c, eV	C/U ²³⁵	Cadmium ratio	Activation ratio
		atom ratio		
Au	1.42	22900	2.09 ± 0.02	1.83 ± 0.02
		5724	1.35 ± 0.01	3.38 ± 0.05
		958	1.07 ± 0.01	7.11 ± 0.05
In	1.33	22900	2.26 ± 0.02	1.87 ± 0.01
		5724	1.46 ± 0.01	3.42 ± 0.04
		958	1.16 ± 0.01	6.78 ± 0.04
Lu ¹⁷⁶	1.45	22900	73.0 ± 2.0	1.22 ± 0.01
		5724	30.0 ± 0.3	1.40 ± 0.01
		958	8.2 ± 0.3	1.05 ± 0.01
Mn	0.729	22900	17.3 ± 0.1	1.000
		5724	5.70 ± 0.05	1.000
		958	1.76 ± 0.02	1.000
Pu ²³⁹	0.619	22900	52.0 ± 1.0	1.12 ± 0.01
		5724	19.4 ± 0.4	1.28 ± 0.01
		958	6.59 ± 0.1	1.27 ± 0.01
U ²³⁵	0.648	22900	35.5 ± 0.8	0.955 ± 0.01
		5724	10.87 ± 0.07	0.862 ± 0.005
		958	2.62 ± 0.03	0.612 ± 0.01

rate should have been observed after the 6-day irradiation, but the actual increase was $< 3\%$. Since several of the cross sections involved in the production are not known, it is not yet possible to conclude which of the predicted cross sections are wrong.

A second exposure of the same sample for 20 days in V-15 has been performed in order to increase the production of Cf²⁵⁴. This time the sample was covered by Cd to shield it from thermal neutrons, the production rate by epithermal neutrons alone being of primary interest. Results of this exposure are not yet available.

Additional samples of Cf²⁵² are on order from Oak Ridge National Laboratory. If the results of the most recent irradiation warrant it, these will be exposed in regions of the HFBR where the flux is entirely thermal and also where there is a large epithermal component, in an attempt to separate

the thermal and epithermal cross sections. Measurements of the production rate as a function of exposure time will also be made in order to gain additional information on the cross sections.

E. WEINSTOCK, J. CONANT

U²³³O₂-ThO₂-D₂O EXPONENTIAL EXPERIMENTS

A set of experiments was conducted to determine reactor physics parameters of D₂O-moderated lattices of uniformly spaced fuel elements containing U²³³ and Th²³². The experiments included both low-multiplication approaches and exponential experiments. In the course of the latter, measurements were made of the material buckling, ζ_{Dy} (dysprosium disadvantage factor), ρ^{02} (ratio of epi- to subcadmium capture ratio in Th²³²), and δ_{23}^{02} (ratio of fission in Th²³² to fission in U²³³). Preliminary results from the exponential experiments are summarized in Table 5.

In the experiments, "kilorod" fuel elements were used; these are 1/2-in.-o.d. Zircaloy-2 tubes with 0.035-in. wall thickness containing particles of 3% U²³³O₂-97% ThO₂ made by the sol gel process, and compacted by vibration to a density of 8.96 g/cc. The active length of the fuel is 42 1/2 in. These fuel elements were loaded into a D₂O-filled tank with a 29.687-in. i.d. The tank was radially surrounded by 1/4-in. boral. An additional reflector of 6 in. of paraffin was installed outside the boral for measurements on lattices with pitches of 11.481, 6.510, 3.759, and 2.170 cm. This layer minimized the perturbation due to position-independent return of leakage neutrons.

A low-multiplication approach was carried out for each lattice to establish safe loadings for the subsequent exponential experiments. These approaches provided preliminary estimates of the buckling and the critical mass.

The material bucklings were obtained from measured spatial distributions of the neutron flux, which were found by exposure of In foils along the two principal axes of the cylindrical systems. It was necessary to correct the measured distributions for the effects of photoneutrons from the inherent gamma-ray activity of the U²³² decay chain in the fuel, and also for photoneutrons produced in the D₂O by gamma rays from the source reactor. The data were also corrected for effects of room return when necessary.

The measurement of ζ_{Dy} was made by determining the spatial distribution of activation of 0.047-

Table 5
Material Bucklings, ρ^{02} , ζ_{Dy} , and δ_{23}^{02} of the 3% U^{233} -97% ThO_2 - D_2O Lattices

Lattice No.	Mole % D_2O (± 0.05)	Pitch, cm	B_m^2 , m^{-2}	Mole % D_2O	ζ_{Dy}	ρ^{02} , Cd ratio	ρ^{02} , Thermal activation	δ_{23}^{02}
1	99.25	11.481	11.29 ± 0.20	99.22	1.423 ± 0.017	0.089 ± 0.005		
2	98.95	9.462	14.67 ± 0.37	99.22	1.387 ± 0.015	0.104 ± 0.005		
3	99.34	7.821	19.13 ± 0.27	99.23	1.374 ± 0.013	0.166 ± 0.006		
4	99.25	6.507	22.32 ± 0.14	99.25	1.345 ± 0.012	0.234 ± 0.008		
5	99.33	5.738	25.00 ± 0.16	99.30	1.333 ± 0.015	0.297 ± 0.011		
6	99.30	4.338	28.64 ± 0.29	99.33	1.294 ± 0.016	0.559 ± 0.018	0.634 ± 0.060	0.0047 ± 0.0007
7	99.26	3.758	29.85 ± 0.22	99.20	1.259 ± 0.013	0.780 ± 0.032	0.840 ± 0.058	0.0056 ± 0.0007
8	99.30	2.170	20.54 ± 0.20	99.24	1.173 ± 0.015	5.19 ± 0.54	4.66 ± 0.19	0.0117 ± 0.0008

in.-diam $\times$ 0.005-in.-thick Dy-Al foils across a unit lattice cell. The values of ρ^{02} were found directly from determinations of the Cd ratios of activation of Th. In the three tightest lattices, an independent evaluation of ρ^{02} was made by measurement of the relative activation of Th and Dy.

The measurement of δ_{23}^{02} was made by a new technique. This technique, also discussed elsewhere in this report, makes use of the sensitivity of some plastics to radiation damage by energetically charged particles. Plastic foils are used to record the fissions that occur in adjacent thin films of U^{233} and Th^{232} simultaneously exposed between fuel pellets in flux-symmetric positions in the lattice. The thin films are electrodeposited on 0.25-mm $\times$ 1.08-cm steel or Pt. The thickness of the Th^{232} films is $\approx 200 \mu g/cm^2$, and the thickness of the U^{233} film is $\approx 0.5 \mu g/cm^2$. Alpha-counting of the films provides a precise measurement of their content. The plastic used is Lexan, 0.152 mm $\times$ 1.08 cm.

Each fission that occurs in the thin film causes a damaged area in the plastic and appears as a short track when the plastic is etched in sodium hydroxide. The plastic is then photographed and a 170 $\times$ enlargement is made from which the tracks are counted visually. The relative density of tracks in the two foils is the relative rate of fission in the two thin films.

This technique has the advantage of not requiring calibration using a double fission chamber, as in the case of the technique based on measuring the activity of gross fission products, or elaborate chemistry and reliance upon knowledge of fission product yields, as is required in the method based on separation and counting of single fission products.

The small fission cross section of Th^{232} makes this technique particularly well suited to this fuel. The quantities of Th^{232} and U^{233} electrodeposited can be controlled to provide comparable fission rates in the two thin films. This causes the accuracy of the measurement to be somewhat independent of the value of δ .

G. PRICE,
H. WINDSOR, W. TUNNEY

ANISOTROPY OF NEUTRON MIGRATION

After completion of the measurements of anisotropy of slowing-down in lattices of plates of Al in H_2O , attention was given to the anisotropy of the diffusion length. Experiments were made with the plates alternately arranged parallel and perpendicular to the surface of a thermal column. The attenuation of the flux displayed the expected exponential shape when the plates were parallel to the thermal column. When the plates were perpendicular to the thermal column, however, plots of $\ln \Phi$ vs Z showed continuous curvature over distances corresponding to from 6 to 8 diffusion lengths. This curvature was such that diffusion lengths deduced from the rate of attenuation at the two ends of the distribution could differ by as much as 20%. A number of ancillary experiments were performed to investigate this effect and the problem is currently being investigated theoretically.

P. PALMEDO, J. CONANT

PHYSICS OF FAST SODIUM-COOLED REACTORS

Fast Source Assembly

During the year, the primary interest of the experimental reactor physics group has turned to

fast reactor physics. A major effort in this direction has consisted of the construction of a critical assembly machine (FS-1) that was designed for the operation of solid assemblies; the construction was completed in February 1967.

The FS-1 machine uses one stationary and one movable cart as base plates upon which the cores and reflectors of uranium-fueled critical experiments are loaded. Essentially half the core and half the reflector are loaded onto each cart. The base plates on the carts are granite slabs, each $3 \times 6 \times 1$ ft thick. The movable cart rides on low friction linear bearings that function as wheels. The drive system for the movable cart sends it up an incline formed by cylindrical hardened steel rails imbedded in concrete on the floor. On a scram, the clutch in the drive system is disconnected and the cart rolls downhill.

The rods used to control the reactivity of the system during operation are of the rack and pinion type that has been used for more than two years on Neutron Source Reactors I and II. The rods move horizontally through sections of the core and reflector.

Prior to the operation of the first critical experiment, the steel reflector was loaded onto the carts and the system was thoroughly tested under this load. At this point, the assembly was ready for the loading of fuel to criticality. Fuel loading was not undertaken, however, until operating limits were established and a Safety Analysis Report (SAR) for the Critical Facility was accepted by the AEC. In addition, a separate safety report on the FS-1 experiments was also written and submitted for review by the RCESC. The SAR for the Critical Facility and the safety report on the experiments have now been accepted, and the loading of the first critical assembly has begun.

The fuel for these experiments is the steel-clad uranium foil that was used by Livermore for the hot box critical experiments, in the Pluto project. The cores to be assembled will consist of uranium, graphite, and steel, in proportions that provide median fission energies comparable to those in large LMFBR's. The assemblies have provisions for subregions of varying cell structure in the center that will be used for studying the effects of heterogeneity. They also provide for extraction of neutron beams for spectral studies, and for the study of measurements of reactivity coefficients through use of a pile oscillator.

A. COURT,
K. DOWNES

Fast Neutron Spectroscopy

In connection with construction and planned use of the FS-1 facility, a program has begun to construct proton recoil counters filled with both hydrogen and methane, and to explore the features that limit the accuracy and resolution of fast neutron spectra obtained with such counters. During the past year, several proton recoil counters have been constructed, and notable progress has been made toward understanding the capabilities and limitations of the method.

It was found that the methane supplied through commercial channels was not pure enough for use in proton recoil counters. This observation was found to apply even to methane that had been specially purified. It was therefore necessary to construct a filling system for methane-filled counters, equipped specifically to provide additional purification. The purifier consists of a molecular sieve and a BTS copper catalyzer. Use of this system has consistently reduced the content of the filling gas in water vapor and oxygen to a fraction of a part per million. It was also found necessary to clean the counters carefully with a series of solvents and to bake them prior to filling, so as to eliminate trace amounts of material such as soldering flux that were deposited during manufacture. All variability of resolution that accompanied differing levels of impurity of the gas has now disappeared.

A residual departure of observed resolution from the theoretical value has been traced to a variability in diameter of the fine central collector wire. This produces a noncylindrical electric field to accelerate the electric charge, and thus a nonconstant gas multiplication for a fixed number of ion pairs. Special wire has been procured commercially. This wire is drawn through a carefully fabricated diamond die and is much more uniform than that commonly used in proton recoil counters; it has been incorporated as the central conductor in locally made counters.

With the care described above, it has been found possible to obtain systematically a resolution of better than 4% in methane-filled counters, at the 615-keV line obtained by using the $N^{14}(n,p)C^{14}$ reaction with thermal neutrons.

For the next stage of this test of ability to produce systematically good resolution, counters of standard design are being procured commercially. These counters are filled prior to receipt and are refillable, so that the effect of improvement of fill-

ing procedures can be tested. Half will be made with standard central wires, and half with the special wire described above. Thus this aspect of control on resolution can also be tested.

In a separate experiment, the linearity of response of methane counters was tested by using monochromatic neutrons produced at the Brookhaven Van de Graaff. The linearity was excellent, and the energy calibration through the $N^{14}(n,p)C^{14}$ reaction was precisely confirmed.

In another set of experiments, the spectrum of rise times of pulses produced by monoenergetic gamma rays in the counter has been investigated. It was found that, contrary to common assumption, the spectrum of rise times is a function of the energy of the gamma rays. This dependence introduces an uncertainty into the subtraction of background of gamma-induced events by pulse-shape discrimination. The effect is being investigated further to establish how this subtraction can still be done.

The contribution to the rise-time spectrum by neutrons not completely stopped in the active volume of the counter is another source of ambiguity. This is also being studied, both experimentally and theoretically.

C. SASTRE

Analysis of Spectrum Measurements With Proton Recoil Counters

During the year, various techniques for analyzing proton recoil data have been investigated, and an improved method of deriving neutron spectra from such data has been established. The analysis proceeds in three steps. First, the response matrix (neutron to pulse) is calculated for the counter and gas mixture used. This response matrix includes the perturbing effects of the walls and ends of the counter (wall effects and end effects). A code entitled JERICHO has been written to calculate the response matrix. In the second step, the output from the multichannel analyzer in the counting system, which is a plot of the rise time against the energy of the pulses, is converted to a spectrum of number of proton pulses against energy. This is done by subtraction of the gamma-ray background. In the third step, the response matrix is used to calculate the neutron spectrum from the pulse spectrum by use of a method of least squares with variable restraints. This calculation is performed by the code ESLUP. The two computer codes are currently undergoing final testing.

P. PALMEDO

Fission Track Detectors

A study of the applicability of plastic fission track detectors [J.W.N. TUYN, Solid state nuclear track detectors in reactor physics experiments, *Nucl. Appl.* 3, 372 (1967)] to precise measurements of fission rate has been undertaken. The technique has several advantages. It can be used without introducing appreciable perturbations in the flux, and it makes possible point measurements of the fission rate, in contrast to the small fission chambers usually used for such measurements. Because of the finite size of counters, these perturb the flux in an unknown way and average the fissions over a region of uncertain size. The technique using plastic foils also integrates over the time, and thus can be used at low flux levels. This feature presents an advantage over methods based on activation.

The detectors have consisted of 0.004-in.-thick Lexan (polycarbonate) plastic placed next to a thin U^{233} deposit previously assayed by alpha counting. These sandwiches have been exposed on a rotating wheel in a graphite thermal column at the Medical Research Reactor (MRR), together

Figure 6. Fission tracks in etched plastic.

with 0.005-in.-thick Au foils. The thermal flux deduced from the activity of the Au is used to compute the fission rate in the U^{233} deposit. After exposure, the plastic is etched in NaOH, and the track density is measured by microscopic scanning. With an etching time of 10 min in 6.5 *N* NaOH solution, it was found that the over-all efficiency of the detector was $\approx 97\%$. A reduction of the etching time to 8 min has resulted in improved track resolution and also increases the efficiency of track registration to very close to 100%. Figure 6 shows an enlargement of a portion of one of the etched plastic foils.

The possibility of performing the scanning automatically, and thus greatly reducing the time and labor of visual microscopic scanning, is being investigated. Several problems must be met in automation of counting, but it appears that all can be solved. Among the principal ones are the following. Corrections must be made for tracks that intersect and are counted as a single track. This correction resembles the standard one for resolving time when counters are used. Tracks that penetrate the plastic normal to the surface are less readily counted. Some background is introduced if the counting system misidentifies scratches and other blemishes on the plastic.

Extension of the technique to measurement of (n, α) reactions is foreseen for the future.

W. TUNNEY, E. WEINSTOCK

Fine Structure in Fast Reactor Cells

Components have been obtained for assembling wafer-type cells to fill a subregion of the FS-1 assemblies. These components consist of plates of aluminum, graphite, stainless steel, U^{235} , and low-enrichment uranium. The experiments using these cells are to be conducted after the spectrum in the assembly is measured by proton recoil techniques and by activations. The composition of the cells will be chosen to match as closely as possible that of the surrounding driver region. Detailed measurements of the fine structure of reaction rates will then be made with varying thicknesses and arrangements of the components of cells.

The U^{235} plates to be used were obtained on a no-cost basis as surplus from ORNL.

P. PALMEDO, J. CONANT

Prompt Neutron Lifetime

A review of sources of error in measured values of the neutron lifetime in fast critical experiments indicates that one of the principal uncertainties

arises from incomplete knowledge of the energy distribution of the delayed neutrons. The effect appears through inadequate capability to convert true yields of delayed neutrons to effective yields, and thus an uncertainty in interpreting measurements of β/l as measurements of l .

A measurement suggested by G. Brunson offers the possibility of measuring the energy spectra of the delayed neutrons from fission to the desired accuracy. The need for and suitability of such an experiment are being investigated further, and the possibility of obtaining the necessary components is being explored.

P. PALMEDO, J. CONANT

Exponential Experiments With Pu-Al Rods in D_2O

A series of exponential experiments has begun that uses Pu-Al rods in heavy water containing high concentrations of boron and cadmium salts. These thermal neutron poisons suppress fission by low-energy neutrons and cause the criticality to depend strongly on values of the capture-to-fission ratio (α) of plutonium for neutrons of higher energies. The fuel rods consist of an alloy of 10 wt % Pu in Al, 0.600 in. in diam, and are clad in Zircaloy-2 tubing with an o.d. of 0.668 in. and a wall thickness of 0.028 in.

The experiments were first conceived to provide values of α of plutonium over broad energy regions for use in calculations of the neutronics of thermal reactors. They promise, however, to have greater value for the LMFBR program, where it has been observed that these important quantities are currently unknown to within a factor of 1.5.

As a preliminary step in these experiments, it has been necessary for safety purposes to find the criticality of the fuel in light water. Therefore, six subcritical lattices were constructed of the Pu-Al rods in ordinary water, with volume ratios of water-to-fuel ranging from 1.0 to 11.4. The material buckling, B_m^2 , was measured to moderate accuracy by In foil activations at a single fuel loading in each lattice. In addition to supplying data needed for safe handling and storage of the fuel, the measurements provide new points in criticality data libraries.

Cadmium rods were placed around the fueled region to isolate it from the H_2O reflector, since the presence of the reflector perturbed the radial flux distributions for a considerable distance into the small cores. Radial flux distributions were measured with the cadmium rods in place, while axial flux distributions were measured both with

and without cadmium rods. From these data the material buckling and the reflector savings could be inferred.

The data indicate that the minimum critical loading is 68 fuel rods and the minimum critical diameter is 28 cm. It was therefore decided that fuel should be stored and transported in containers containing 34 or less rods, and in arrays of isolated cylinders, each <20 cm in diam.

Calculations made with the HAMMER code provide values of B_m^2 in H_2O that differ from observed values by $\approx 8 \text{ m}^{-2}$, in a range of buckling from 30 to 135 m^{-2} .

Loading of the lattices of rods in heavy water has now begun. The high reactivity of this fuel makes it necessary to assemble the experimental lattices with more than normal caution.

G. PRICE, H. WINDSOR

SUPPORT WORK FOR EXPERIMENTS

Neutron Source Reactors I and II

The two neutron source reactors (NSR I and II) at the Critical Facility were available for experiments $>90\%$ of the past year. In all, 453 runs totaling 10.23 MWh were carried out with NSR I. These runs were made to supply neutrons for experiments using U^{233} - Th^{232} rods in D_2O , and others using Pu-Al rods in H_2O and D_2O . Some evidence of deterioration of fuel in NSR I has appeared through an increase in activity of the coolant water. The levels are still very low, however, and they are being monitored to establish whether the deterioration will continue.

In conjunction with the studies on anisotropy of neutron migration, 214 runs totaling 14.91 MWh were carried out with NSR II.

A. COURT,
K. DOWNES

Control of Fissionable Material

Eighteen different types of fuel materials are currently available at the Critical Facility for use in critical and exponential experiments. Information on the inventories and locations of eleven of these materials has been entered into a system of computerized control that maintains journal and ledger entries for each material. The system now encompasses all of the highly enriched material on hand, leaving only the material of lower enrichment to be incorporated in the coming months.

A. COURT, K. DOWNES

Criticality Calculations

It has become necessary to provide within the experimental group a capability of calculating the criticality of certain classes of fast neutron assemblies. Typical requirements include initial estimates of the criticality of the FS assemblies, safety of performance of fast critical experiments, and the safe storage of large amounts of fuel for fast neutron critical experiments.

As a first step toward providing the necessary computational capability, a study of the limitations of a BNL version of AIM6 is being made. Comparisons have been made between calculated and observed criticality of Godiva and the SORA experiment.

Taking into account the differences between observed and calculated criticality in the above cases, calculational surveys have been made of the effects of hydrogenous reflection of the FS-1 critical experiments and the Pulsed Fast Reactor criticals, as well as estimates of neutron multiplication by stored fuel under conditions of complete water flooding.

A. COURT, K. DOWNES

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National Neutron Cross Section Center

S. PEARLSTEIN

In May 1967 approval was obtained from the Research Division and Reactor Development and Technology Division of the USAEC to merge the cross section compilation and evaluation activities of the Nuclear Engineering Department. This new activity is called the National Neutron Cross Section Center (NNCSC) and combines the Neutron Cross Section Compilation Center (Sigma Center) and the Cross Section Evaluation Center. These Centers formerly operated within the Reactor Physics Division. On September 15, 1967, the merger was effected with the appointment of a Deputy Director who would also function as Acting Director. The functions of the NNCSC are to develop a highly computerized system for the storage and retrieval of cross section information, and to advance new methods of cross section analysis.

PUBLICATION OF NEUTRON CROSS SECTIONS

Volume IIC ($Z=61$ to 87), Supplement 2, of BNL 325 was published and distributed. This completed the printing and distribution of all supplements to the second edition of *Neutron Cross Sections*. Studies are under way to automate future compilations of neutron cross sections and angular distributions. If this procedure proves successful, editions and supplements of compiled cross sections will be produced more frequently.

DATA STORAGE AND RETRIEVAL

The cross section files are almost completely contained in SCISRS, the Sigma Center Information Storage and Retrieval System. This system, programmed for the IBM 7094, allows for rapid encoding and retrieving of the data. The updating of the SCISRS tape with new and old data continues. The present system contains $>1,000,000$ data points.

An adjunct system is a complete bibliographic record to the data. A modified NBS-SYX Program (W.W. Youden and F. Sauber, NBS-SYX, National Bureau of Standards, Washington, D.C.)

was adapted to the Center's specific needs. It provides alpha-numerical sorted listings of authors, laboratories, references, isotopes, and subjects as options. A newsletter in two parts has been completed and distributed [*SCISRS Newsletter, Part A, Reference and Bibliography*, BNL 50061A (L-391); *SCISRS Newsletter, Part B, Isotope Listing*, BNL 50061B (L-391)].

A new system, SCISRS II, is being considered that will contain integrated, though separated, bibliographic and data libraries for experimental results. This program will be broadened in scope over SCISRS and will be written in a language compatible with major computer facilities.

The collaborative program with the Neutron Data Compilation Centre (CCDN) at Saclay is continuing. Through this program, experimental data obtained in European Nuclear Energy Agency countries are placed in SCISRS format by the CCDN. An exchange of data tapes takes place between the CCDN and NNCSC.

EVALUATED NUCLEAR DATA FILE

The Evaluated Nuclear Data File, developed by H. Honeck, is divided into two parts, ENDF/A and ENDF/B.

Specifications for ENDF/A are described in the report BNL 8381 entitled "Evaluated Nuclear Data File Description and Specifications," by H. Honeck. The file currently contains UKAEA, KAPL, and GA data. Additions are made whenever significant data are received in the ENDF/A format.

Specifications for ENDF/B are contained in the report BNL 50066 entitled "ENDF/B - Specifications for an Evaluated Nuclear Data File for Reactor Applications," by H. Honeck. ENDF/B is a cooperative effort among U.S. laboratories organized by the USAEC Division of Reactor Development and Technology and coordinated by the Cross Section Evaluation Center at BNL. It is the objective of the participants (the Cross Section Evaluation Working Group) to assemble a library

of recent evaluations for materials of interest to reactor designers. The materials now included in the system are listed in Table 1 together with the laboratory responsible for the selection of data. New materials are being added. The laboratories and the active members of CSEWG are listed in Table 2. Table 3 summarizes the characteristics of ENDF/A and ENDF/B.

ENDF material is available to U.S. users from the NNCSC at BNL and to ENEA countries from CCDN. Others can receive data from BNL provided bilateral agreements exist for the exchange of neutron data or USAEC approval can be obtained. The ENDF/B materials that have cleared preliminary checking procedures and are available for distribution are listed in Table 4.

The ENDF/B library was assembled to increase the amount of cross section data in a single format available to the reactor designer. Because of the tight schedule of completing the file, the data may contain errors and may not include the most re-

cent evaluations. An iterative philosophy is used concerning ENDF/B. Periodically—perhaps annually—the file will be revised as errors become known and new data become available. For some materials, several revisions, or several years, may be necessary before ENDF/B will constitute a good set of data. In the meantime, the completeness of the file suggests that it can be used as a reference set of data for reactor calculations.

TRANSURANIUM CROSS SECTIONS

In order to calculate the buildup of transuranium isotopes in a high flux epithermal reactor, it is important to know the thermal neutron capture and fission cross sections and the capture and fission resonance integral of each isotope in the chain. Since experimental data are very sparse and the required resonance parameters used in the calculations are lacking, it was necessary to approach the problem from a systematic viewpoint.

Table 1

ENDF/B Data

Material	MAT	Laboratory	Material	MAT	Laboratory	Material	MAT	Laboratory
H ¹	1001	BN	Zr ⁹²	1079	BAPL-KAPL	Au ¹⁹⁷	1037	BN
H ₂ O*	1002	GA	Zr ⁹⁴	1080		Th ²³²	1038	BW
D ²	1003	BN	Zr ⁹⁶	1081		Pa ²³³	1040	BAPL
D ₂ O*	1004	GA	ZrH*	1023	GA	U ²³³	1041	GA-ORNL
Li ⁶	1005	LASL	Nb	1024	GA	U ²³³ F.P.	1042	BW
Li ⁷	1006	LASL	Mo	1025	ANL	U ²³³ F.P.	1066	
Be	1007	GA	Xe ¹³⁵	1026	BN	U ²³³ F.P.	1067	
Be-metal*	1064	GA	Sm ¹⁴⁹	1027	BN	U ²³⁴	1043	GA
BeO*	1008	GA	Eu ¹⁵¹	1028	BN	U ²³⁵	1044	KAPL
B ¹⁰	1009	ORNL	Eu ¹⁵³	1029	BN	U ²³⁵ F.P.	1045	BW
C	1010	KAPL	Gd	1030	ANL	U ²³⁵ F.P.	1068	
Graphite*	1065	GA	Dy ¹⁶⁴	1031	BN	U ²³⁵ F.P.	1069	
CH ₂ *	1011	GA	Lu ¹⁷⁵	1032	BN	U ²³⁶	1046	GA
N ¹⁴	1012	ORNL	Lu ¹⁷⁶	1033	BN	U ²³⁸	1047	BW
O ¹⁶	1013	KAPL	Hf ¹⁷⁴	1082	BAPL-KAPL	Np ²³⁷	1048	ID
Na	1059	APDA	Hf ¹⁷⁶	1072		Pu ²³⁸	1050	AI
Mg	1014	ANL	Hf ¹⁷⁷	1073		Pu ²³⁹	1051	GE
Al ²⁷	1015	ORNL	Hf ¹⁷⁸	1074		Pu ²³⁹ F.P.	1052	BW
Ti	1016	ANL	Hf ¹⁷⁹	1075		Pu ²³⁹ F.P.	1070	
V	1017	ANL	Hf ¹⁸⁰	1076		Pu ²³⁹ F.P.	1071	
Cr	1018	WAPD	Ta ¹⁸¹	1035	GE	Pu ²⁴⁰	1053	APDA
Mn ⁵⁵	1019	BNL	W ¹⁸²	1060	GE	Pu ²⁴¹	1054	GA
Fe	1020	WAPD	W ¹⁸³	1061		Pu ²⁴²	1055	AI
Ni	1021	WAPD	W ¹⁸⁴	1062		Am ²⁴¹	1056	ID
Zr ⁹⁰	1077	BAPL-KAPL	W ¹⁸⁶	1063		Am ²⁴³	1057	ID
Zr ⁹¹	1078					Cm ²⁴⁴	1058	AI

*Thermal data only.

Table 2

Participating Laboratories and Representatives

Laboratory	Representative(s)	Laboratory	Representative(s)
Advisory Committee on Reactor Physics (ACRP)	D. Goldman	Courant Institute – New York Univ. (CI)	M. Kalos
Argonne National Laboratory (ANL)	E. Pennington B. Toppel	General Atomic (GA)	M. Drake D. Mathews A. Profio
Atomic Energy Commission (AEC)	P. Hemmig	General Electric, San Jose (GE-APED)	P. Aline
Atomic Power Development Associates (APDA)	D. Green T. Pitterle	General Electric, San Jose (GE-APO)	P. Greebler
Atomics International (AI)	H. Alter R. Berland C. Dunford R. Hubner	General Electric, Cincinnati (GE-NMPO)	W. Henderson
Babcock & Wilcox Company (BW)	A. Livolsi D. Roy W. Wittkopf	Idaho Nuclear Corporation (ID)	R. Grimesey M. Moore J. Smith
Battelle-Northwest (BN)	R. Liikala B. Leonard K. Stewart	Knolls Atomic Power Laboratory (KAPL)	C. Lubitz
Bettis Atomic Power Laboratory (BAPL)	D. Harris	Los Alamos Scientific Laboratory (LASL)	M. Battat D. Dudziak R. LaBauve
Brookhaven National Laboratory (BNL)	J. Chernick H. Kouts S. Pearlstein A. Prince T. Stephenson J. Felberbaum R. Sher (Stanford)	Oak Ridge National Laboratory (ORNL)	F. Clark C. Craven D. Irving
Combustion Engineering (CE)	L. Noderer	Savannah River Laboratory (SRL)	D. Finch H. Honeck J. Suich
		Westinghouse Atomic Power Division (WAPD)	N. Azziz R. Dannels

Table 3

Characteristics of the Data Files

	ENDF/A	ENDF/B
Basic storage unit	Evaluated point cross section data covering a particular energy range for one reaction type and one material. Highly flexible format.	All evaluated point data for one material needed for a reactor calculation. Simple format.
Type of data included	All reaction types for all incident and final particle types.	Data for neutron-induced reactions required for reactor calculations.
Ordering of data	Data stored in the order received by the ENDF Center.	Ordered by material number, data type, and reaction type.
Selection and revision of data	No selection is made. All data are accepted and added to the master files. Hence many alternative evaluations occur.	One complete set of data for a material will be selected and stored. These data will be updated at regular intervals.
Main usage	Storage of partial evaluations and alternative or older evaluations used as building blocks to generate complete evaluations.	Complete sets of evaluated point data used as direct input to reactor codes or codes to compute multigroup sets.

Table 4

ENDF/B Data Available From NNCSC or CCDN

MAT	Material	No. of cards
1001	H ¹	205
1003	H ²	263
1005	Li ⁶	1263
1006	Li ⁷	1140
1009	B ¹⁰	456
1010	C ¹²	1938
1012	N ¹⁴	3674
1013	O ¹⁶	2380
1014	Mg	502
1016	Ti	650
1017	V	716
1018	Cr	2296
1019	Mn	1326
1020	Fe	3299
1021	Ni	3082
1025	Mo	570
1026	Xe ¹³⁵	386
1027	Sm ¹⁴⁹	897
1030	Gd	601
1035	Ta ¹⁸¹	721
1042	U ²³³ rapidly saturating F.P.	87
1043	U ²³⁴	684
1045	U ²³⁵ rapidly saturating F.P.	87
1046	U ²³⁶	675
1047	U ²³⁸	953
1051	Pu ²³⁹	1008
1052	Pu ²³⁹ rapidly saturating F.P.	87
1053	Pu ²⁴⁰	807
1054	Pu ²⁴¹	2145
1056	Am ²⁴¹	656
1057	Am ²⁴³	436
1059	Na ²³	1330
1060	W ¹⁸²	585
1061	W ¹⁸³	667
1062	W ¹⁸⁴	568
1063	W ¹⁸⁶	530
1066	U ²³³ slowly saturating F.P.	76
1067	U ²³³ nonsaturating F.P.	72
1068	U ²³⁵ slowly saturating F.P.	76
1069	U ²³⁵ nonsaturating F.P.	72
1070	Pu ²³⁹ slowly saturating F.P.	76
1071	Pu ²³⁹ nonsaturating F.P.	72

Following the method of Huizenga et al.,* the barrier penetration nature of the fission process was considered, and a correlation was established between the ratio $\ln(\sigma_f/\sigma_\gamma)$, binding energy B_n , and fission threshold E_f . Thus, knowing either one

of the quantities $(\sigma_f, \sigma_\gamma)$, it is possible to estimate the other.

Based on the logic that the same reasoning applies to the resonance integrals, a similar curve was drawn for $\ln(I_f/I_\gamma)$. From this systematic treatment it is now possible to establish the ratio of I_f/I_γ for all fissionable isotopes; and knowing I_f or I_γ , the other is determined. However, unlike the capture cross sections, virtually no information exists for the resonance integrals of the nuclides of interest.

Upon investigation of the resonance structure of the compound nuclei, it was discovered that one-half the capture resonance integral $I_\gamma/2$ was attained by either the first or third resonance. Those nuclides with the capture integral reaching its fifty percent value within the first resonance form compound nuclei of even-odd nature upon capture of a neutron. Those reaching $I_\gamma/2$ within the third resonance form either an odd-odd or even-even compound nucleus and have even $N-Z$ values. The resonance structure correlation with the capture integral was extended to the B_n-E_a relationship, and $I_\gamma/2$ as a function of B_n-E_a is shown in Figure 1.

From these relationships the thermal fission and capture cross sections and fission resonance integrals were calculated for ${}_{94}\text{Pu}^{242}$, ${}_{95}\text{Am}^{243}$, ${}_{96}\text{Cm}^{244-248}$, ${}_{97}\text{Bk}^{249}$, and ${}_{98}\text{Cf}^{250-254}$. The recommended values are given in Table 5.

CROSS SECTION STATISTICS

The random matrix theory of nuclear cross section fluctuations has been extended to include the possibility of time reversal noninvariance in nuclear forces. It is found that detailed balance in nuclear reaction, which results from time reversal invariance, is obeyed on the average even when time reversal invariance is violated.

The CDC computer program, which calculates the eigenphase angles or random unitary matrices, has been extended to include the calculation of some relevant functions of these angles as well as their statistical averages.

MULTILEVEL ANALYSIS OF U²³⁵ TOTAL AND FISSION CROSS SECTIONS

A final report [D.B. ADLER AND F.T. ADLER, *Multilevel Analysis of the U²³⁵ Total and Fission Cross Sections in the Energy Region Below 37 eV*, BNL 50045 (T-455), March 1967] has been issued of the

*J.R. HUIZENGA AND R.B. DUFFIELD, *Phys. Rev.* **88**, 959 (1952); G.T. SEABORG, *The Transuranium Elements*, p. 242, Yale Univ. Press, 1958; R. VANDENBOSCH AND G.T. SEABORG, *Phys. Rev.* **110**, 507 (1958); E.K. HYDE, I. PERLMAN, AND G.T. SEABORG, *Nuclear Properties of the Heavy Elements*, Vol. III, Prentice-Hall, Inc., 1964.

multilevel fitting of U^{235} cross sections. This work was performed at the University of Illinois under subcontract sponsored by the Cross Section Evaluation Center at BNL.

The method applied is based on the multilevel-multichannel formalism, which is recast into a generalized Kapur-Peierls expansion. These formulae express the cross sections as superpositions of interfering Breit-Wigner type lines. The parameters defining the cross sections are obtained by a least squares analysis of the experimental data.

Table 5				
Recommended Values for Capture and Fission Neutron Cross Sections and Capture and Fission Resonance Integrals				
Nuclide	σ_γ , b	σ_f , b	I_γ , b	I_f , b
$^{94}\text{Pu}^{242}$	30	3.5×10^{-2}	1150	0.6
$^{95}\text{Am}^{243}$	180	4.5×10^{-1}	1400	1.5
$^{96}\text{Cm}^{244}$	10	2.7	650	72
$^{96}\text{Cm}^{245}$	335	1900	133	345
$^{96}\text{Cm}^{246}$	15	0.23	2800	18
$^{96}\text{Cm}^{247}$	180	1026	200	492
$^{96}\text{Cm}^{248}$	6	4.5×10^{-3}	600	0.2
$^{97}\text{Bk}^{249}$	500	2.8	1850	5
$^{98}\text{Cf}^{250}$	1500	335	940	85
$^{98}\text{Cf}^{251}$	1100	3000	172	445
$^{98}\text{Cf}^{252}$	30	0.17	1800	5
$^{98}\text{Cf}^{253}$	40	33	540	198
$^{98}\text{Cf}^{254}$	2	8.6×10^{-2}	1650	28

Figure 1. Correlation of $I_\gamma/2$ with $B_n - E_a$ (cut off energy = 0.5 eV)

The data of several useful experiments were considered, and good fits were obtained to the total and fission cross section below 37 eV.

OPTICAL MODEL CALCULATIONS OF LEAD

Sets of optical model parameters have been found which give good fits to the 1.0-MeV experimental cross sections (total and elastic angular distributions) for $\text{Pb}^{208,207,206}$, respectively. These sets are:

	Pb^{208}	Pb^{207}	Pb^{206}
V_{RE} (MeV)	50	50	50
V_{IM} (MeV)	2.0	3.0	3.0
V_{SR} (MeV)	7.0	11.0	12.0
R_0 (fermi)	1.200	1.200	1.200
a (fermi)	0.55	0.55	0.55
b (fermi)	1.0	1.0	1.0

HOLMIUM TOTAL NEUTRON CROSS SECTION

Resonance parameters for 46 resonances of holmium below 235 eV, selected from the literature and from values compiled and recommended in BNL 325, are used as the starting point in fitting the total neutron cross section data to a Breit-Wigner multilevel scattering and single level absorption formula. The addition of two bound levels, one for each s -wave spin state, yields a calculated ratio of thermal neutron capture cross sections for the two spin states which agrees with experiment ($\approx 60\%$ for $J=3$), as does the calculated value of the thermal capture cross section, 67 b. In addition, the two bound levels enable the fit of the total cross section data to be extended to very low energies (0.2 mV). The energy dependent paramagnetic scattering cross section (23.5 b at 0.0253 eV) and the capture and scattering resonance integrals have also been calculated (≈ 603 and 93 b, respectively). M. GOLDBERG, M. BHAT, D. CULLEN, L. HJÄRNE, T. KRIEGER, B. MAGURNO, V. MAY, S. MOORE, S. MUGHABGHAB, A. PRINCE, F. SCHEFFEL, U. SCHULZE, J. STEHN, T. STEPHENSON, L. STRÖMBERG, P. TU

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Evaluation and Technical Assistance Group

C.J. RASEMAN

Study of the U.S. Civilian Nuclear Power Industry

The Division of Reactor Development and Technology (RDT) of the U.S. Atomic Energy Commission is engaged in a detailed evaluation of the technical and economic viability of various power reactor systems in the nuclear power economy projected to the year 2020. For this purpose seven task forces were formed to study the various reactor concepts or to perform assessments of specialized facets of the nuclear power economy. The results of task force analyses will provide an overall evaluation of the future growth and potential of the U.S. civilian nuclear power program, an assessment of the conservation of national nuclear resources, and a guide to research and development needs in reactor technology.

BNL personnel have participated in three of the task forces, whose work is described below.

1. Thorium systems. In this area BNL personnel constituted the working group. The objectives were (a) to make a detailed review of the molten-salt breeder reactor concept, including an evaluation of the technical and economic potential and the necessary research and development, and (b) to assess the role of thorium in the civilian power economy in coming years. Reports on both topics have been written and submitted to the AEC.

2. Advanced converters. The work of this task force consists of study and evaluation of reactors, such as heavy-water-moderated, organic-cooled converters and high-temperature, gas-cooled systems, capable of commercial power generation before the advent of fast breeders.

3. Systems analysis. This task force has combined the information from the various task forces with a mathematical model of the expanding U.S. electric power system, and the simulated economy was optimized by linear programming techniques. The results obtained include (a) the most economical reactor-type mix, (b) the necessary separation-fabrication-processing capacity, (c) the impact on

utilization of natural resources, and (d) the required mining capability. BNL personnel were members of the Research and Development Committee of this task force.

L. EPEL, F. MILES,
C. RASEMAN, H. SUSSKIND

Evaluation Studies

REVIEW OF LIQUID-METAL FAST BREEDER REACTOR PROGRAM PLANS

The Liquid-Metal Fast Breeder Reactor Program Office at Argonne National Laboratory has the responsibility of projecting 10-year program plans leading to the introduction of a fast breeder reactor. At the request of the Division of Reactor Development and Technology, these program plans are evaluated by a number of people at BNL as the drafts are made available.

The program plans are issued in ten sections, and to date BNL has received and commented on seven sections, as follows:

- Section 3 – Components
- Section 4 – Instrumentation and control
- Section 5 – Sodium technology
- Section 6 – Core design
- Section 8 – Fuel recycle
- Section 9 – Physics
- Section 10 – Safety

L. EPEL, F. MILES, C. RASEMAN, H. SUSSKIND

HFBR ANTICRITICAL GRID AND REACTIVITY

The steel grid at the bottom of the core tank of the High Flux Beam Research Reactor suffered the loss of a 90° arc of one rod of the grid during the first year of operation of the HFBR. Since the grid had been placed there (below the core structure) to act as a poison in the event of a core meltdown, there was concern regarding the potential loss in poison that might correspond to this reduction in grid size. Accordingly, some multigroup, diffusion-theory calculations were performed to

estimate the effect of reduced poison on the reactivity of the system for various meltdown conditions.

Calculations were made for a range of dilutions of molten fuel in heavy water, including zero dilution (i.e., it was assumed that the fuel might collect in a lumped mass at the bottom of the vessel following meltdown). In all cases it was shown that the removal of the amount of steel that had been experienced up until that time would not affect the poisoning characteristics of the grid significantly. The Reactor and Critical Experiments Safety Committee decided to have an alternative mechanical design of an anticritical grid available, in case of further failure of the present grid.

L. EPEL

MAGNETOHYDRODYNAMICS

Static screening tests of refractory metal and fuel specimens in pure nitrogen at 1930°C (3500°F) were completed at the General Electric Company's Nuclear Materials and Propulsion Operation. The results are presented in the Radiation Division section, under the heading Exploratory Research and Development.

The parametric studies were discontinued because of the press of work on the Thorium Systems Task Force evaluations.

H. SUSSKIND

TASK FORCE REPORT EVALUATIONS

One of the products of the AEC-RDT Task Force effort on assessing the power reactor economy is the comprehensive appraisal of the various reactor systems. Each major reactor concept competing for viability in the economic climate of the U.S. is being evaluated on a technical and economic basis by the various task forces at BNL, the other National Laboratories, the AEC, and private companies. The results of these studies are published in reports by the working groups performing the studies.

The drafts of the studies that have been reviewed by BNL include those for four reactor types:

1. Light-water reactor: Current Status and Future Technical and Economic Potential of Light Water Reactors.

2. Heavy-water-moderated, organic-cooled reactors: An Evaluation of Heavy-Water-Moderated

Organic-Cooled Reactors, and Supplements A and B.

3. Heavy-water-moderated, boiling light-water reactors: An ORNL Evaluation of an AECL-Proposed 1000 MW(e) HWBLW.

4. High-temperature, gas-cooled reactors: An Evaluation of High-Temperature Gas-Cooled Reactors. L. EPEL, C. RASEMAN, H. SUSSKIND

Joint India-USA Study

In April 1967 representatives of the USAEC and the Indian AEC agreed that the United States would supply the Indian Government with technical data on reactor systems being generated by the U.S. Task Forces.

The BNL commitments in supplying information involve (1) estimates of plant size vs capital costs for sodium-cooled fast breeders in the power range of 150 to 1000 MW(e), and (2) the release of evaluated technical and economic data on the molten-salt breeder reactor.

J. CHERNICK,

L. EPEL, C. RASEMAN, H. SUSSKIND

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Chemistry Division

R.H. WISWALL, JR.

High Temperature Chemistry

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T. TIDWELL, R. TIVERS, J. VAN NORMAN,
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DOUBLE-LAYER STUDIES OF LIQUID METAL-MOLTEN SALT INTERFACES

Experiments have been started to measure double-layer capacitances in molten salt systems by using a dropping bismuth electrode. Results from these measurements are significant for the study of electrode processes and electrode kinetics in molten salt systems. It is also hoped that results from these experiments will be helpful in obtaining a model for the structure of the double layer and also possibly yield data on the existence of complex ions in molten salts after the kinetics of certain electrode processes are measured.

Previous work in this field at high temperatures has been done mostly by the Russian school [E.A. UKSHE, N.G. BUKUN, D.I. LEIKIS, AND A.N. FRUMKIN, *Electrochim. Acta* **9**, 431 (1964)] and some has been done at Imperial College (A.D. GRAVES, G.J. HILLS, AND D. INMAN, *Advances in Electrochemistry and Electrochemical Engineering*, Vol. 4, pp. 117-83, Interscience Publishers, New York, 1966; A.D. GRAVES, private communication, August 1967). No work has been done to date with a dropping metal electrode. Since dropping electrodes have proved most fruitful for similar studies in aqueous electrolytes [D.C. GRAHAME, *Chem. Rev.* **41**, 441 (1947)], and since we have had previous experience with a dropping bismuth electrode [R.J. HEUS AND J.J. EGAN, *J. Electrochem. Soc.* **107**, 824 (1960)], this technique is being extended to capacitance studies.

The apparatus used for producing the bismuth drops is shown in Figure 1. The capacity measurements are made between the bismuth drop and the large cylindrical graphite electrode. Since the capacity of this electrode is many times greater than that of the microelectrode and the two are in

series, one obtains the capacity of the microelectrode-molten salt interface directly.

Measurements are made with a General Radio 1650-A bridge in conjunction with a Tektronix oscilloscope. Since the bismuth drop is constantly changing its area and thus its capacitance, one transfers the degree of unbalance of the bridge onto the oscilloscope. With the help of a photograph

Figure 1. Diagram of cell used for capacitance measurements at dropping bismuth-fused salt interface.

Figure 2. Capacitance of a dropping bismuth electrode at varying potentials in equimolar LiCl-KCl at 475°.

of the envelope obtained, one can calculate the exact area of the drop at the point of balance of the bridge. This is a standard procedure for these measurements, first used by Grahame [D.C. GRAHAME, *J. Am. Chem. Soc.* **71**, 2975 (1949)]. Preliminary measurements have been made on an equimolar mixture of LiCl-KCl at 475°C purified under HCl and filtered. There was no frequency dispersion of capacitance found between 5 and 15 kc, contrary to results of the Russian school. The double-layer capacity at various potentials with respect to a bismuth pool is shown in Figure 2.

Future measurements will be made using a LiCl-KCl eutectic instead of an equimolar mixture so that results can be compared with other measurements. Also, the salt will be electrolyzed between graphite electrodes before use; and an apparatus has been made of Vycor so that measurements can be extended to higher temperatures. Other reference half cells (i.e., Ag, AgCl) will be used so that the exact electrocapillary maximum (capacitance minimum) can be compared with other experiments.

TRANSPORT IN MOLTEN SALT MIXTURES

The internal transference numbers of the cations relative to the chloride ions in the mixture CdCl₂-LiCl were obtained by the method previously described [BNL 50023 (S-69)]. The cell used was

Table 1

Transference Numbers of Lithium and Cadmium Ions Relative to Chloride Ion in the System LiCl-CdCl₂ at 650°C

x_{LiCl}	a_{LiCl}	$E_{\text{cell I}}$	Volts	t_{Li^+}	$t_{\text{Cd}^{++}}$
0.1	0.061	0.0390	0.0385	0.094	0.906
0.2	0.135	0.0352	0.0346	0.186	0.814
0.3	0.218	0.0314	0.0311	0.271	0.729
0.4	0.323	0.0265	0.0270	0.387	0.613
0.5	0.436	0.0224	0.0213	0.489	0.511
0.6	0.554	0.0178	0.0168	0.590	0.410
0.7	0.686	0.0118	0.0115	0.690	0.310
0.8	0.800	0.0075	0.0064	0.791	0.209
0.9	0.900	—	0.0034	0.895	0.105

and the results are presented in Table 1.

THERMODYNAMIC PROPERTIES OF MOLTEN CeCl₃ MIXTURES BY ELECTROMOTIVE FORCE MEASUREMENTS

The free energies of mixing were determined for mixtures of LiCl-CeCl₃ and KCl-CeCl₃. Electromotive force (emf) measurements were used employing either Cl₂ or H₂-HCl gaseous electrodes. The H₂-HCl electrodes are useful when one of the molten salts can exist in two oxidation states. If the lower oxidation state is not stable in a chlorine atmosphere, it can often exist in a H₂-HCl atmosphere. Thus, measurements were carried out on cells such as:

Table 2 gives the results.

HALOGEN-METAL HALIDE SOLUTIONS

The study of the solution chemistry of halogen gases dissolved in their respective molten halides was continued. A more accurate technique for determining the solubility of chlorine in molten chlorides was developed, which showed that the solubility of chlorine in lead chloride at 535°C stated

Table 2
Thermodynamic Properties of LiCl-CeCl₃ and KCl-CeCl₃ Mixtures at 825°C

x_{LiCl}	emf, V	LiCl-CeCl ₃				
		$-F_{\text{LiCl}}^M$	$-F_{\text{LiCl}}^E$	$-F^E$	$-F_{\text{CeCl}_3}^E$	a_{LiCl}
0.10	0.2886	6,657	1,634	163	0	0.0473
0.20	0.2190	5,052	1,541	316	10	0.0987
0.30	0.1703	3,928	1,301	451	86	0.165
0.40	0.1351	3,116	1,117	554	178	0.239
0.50	0.1012	2,334	822	620	417	0.343
0.60	0.0766	1,767	653	634	605	0.445
0.70	0.0468	1,080	302	583	1,238	0.610
0.80	0.0268	618	131	458	1,767	0.753
0.90	0.0101	233	3	247	2,545	0.899

x_{KCl}	emf, V	KCl-CeCl ₃				
		$-F_{\text{KCl}}^M$	$-F_{\text{KCl}}^E$	$-F^E$	$-F_{\text{CeCl}_3}^E$	a_{KCl}
0.10	0.572	13,200	8,185	868	55	0.0023
0.20	0.463	10,675	7,165	1,609	230	0.0075
0.30	0.391	9,015	6,388	2,251	477	0.0160
0.40	0.318	7,335	5,337	2,760	1,042	0.0345
0.50	0.246	5,684	4,175	3,078	1,984	0.0740
0.60	0.175	4,025	2,911	3,141	3,486	0.158
0.70	0.101	2,330	1,550	2,869	5,942	0.344
0.80	0.048	1,115	627	2,247	8,726	0.60
0.90	0.016	375	146	1,278	11,461	0.842

in the previous report [BNL 50023 (S-69)] was in error.

By using the improved technique, the solubility of chlorine in molten AgCl, PbCl₂, and LiCl-KCl eutectic was determined and for the last two systems the solubility was determined as a function of temperature. The results obtained are given in Table 3.

A plot of log mole fraction ($\log x_{\text{Cl}_2}$) vs $1/T$ should be linear with slope equal to $-\Delta H/2.303R$, where ΔH is the heat of solution of chlorine in the molten metal halide. Figure 3 shows such plots for PbCl₂ and the LiCl-KCl eutectic. The ΔH values calculated from the plots are +3.7 kcal/mole for the LiCl-KCl eutectic and +9.4 kcal/mole for the PbCl₂, values similar to those found in the literature for Cl₂ in other mixtures and in pure metal chlorides.

The electrochemistry of chlorine dissolved in the molten chlorides was studied in detail. Cathodic chronopotentiograms were obtained at a dense graphite electrode (density 1.9) for the re-

duction of dissolved Cl₂ to Cl⁻ ion. The results obtained could be interpreted as the reversible two-electron reduction of Cl₂ in solution. However, if this were the case, the diffusion coefficients calculated for all systems were $\approx 10^{-1}$ cm²/sec larger by four orders of magnitude than those generally found for species in molten salts.

In order to more fully understand the electrochemistry of these melts, the technique of polarography was employed. A "pilot ion" experiment was performed wherein the polarograms of both dissolved Cl₂ and Ag⁺ ion in the LiCl-KCl eutectic were obtained in the same experiment. The relative amounts of chlorine and silver ion in the eutectic were known, and the diffusion coefficient of Ag⁺ was known from independent measurements. It was thus shown that the diffusion coefficient of dissolved chlorine in the LiCl-KCl eutectic was of the order of magnitude of 10^{-5} cm²/sec.

The results of the chronopotentiometric experiments must therefore be reinterpreted in terms of either adsorption of Cl₂ on the surface or adsorp-

Table 3
Solubility of Chlorine in Fused Salts

Salt	Temperature, °C	Solubility	
		Moles/cc	Mole fraction
AgCl	518	2.31×10^{-7}	6.85×10^{-6}
PbCl ₂	513	0.52×10^{-7}	2.95×10^{-6}
	535	0.64	3.62
	585	0.78	4.45
	630	1.05	6.12
	639	1.11	6.47
LiCl-KCl	400	1.26×10^{-7}	4.19×10^{-6}
	450	1.46	5.21
	500	1.70	5.83
	550	2.06	7.14

tion in Cl₂ in the pores of the graphite (void volume in the graphite is $\approx 10\%$). Further experiments are needed to obtain chronopotentiograms at a nonporous electrode, such as pyrolytic graphite, in order to calculate accurate diffusion coefficient values.

Experiments have been started on the solution chemistry of bromine dissolved in molten metal bromides. A heated enclosure has been built to maintain the experimental cells, gas lines, and a bromine generator at a temperature above the boiling point of bromine (58.78°C). Preliminary experiments show that bromine is appreciably more soluble in bromides than chlorine in similar chloride systems.

Fluorocarbon Studies

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V. WILSON, W. RIEL

PYROLYSIS OF PERFLUOROBICYCLOHEXYL (C₁₂F₂₂)

Pyrolytic studies with this compound are of considerable interest because it is unusually sensitive thermally compared to all the other fluorocarbons worked with here. Two distinct lines of attack have been followed: (1) a kinetic study following rate of disappearance of starting compound at a series of temperatures, and (2) isolation and characterization of the principal products in the complex mixture formed.

Figure 3. Solubility of chlorine in fused salts.

The kinetic studies were carried out at 350°, 360°, 370°, 377°, and 385°C with the C₁₂F₂₂ vapor at a pressure of ≈ 1.5 atm. Prefluorinated Monel cells and sampling volumes were used throughout. The decomposition was first order at all temperatures, as shown by the least squares lines in Figure 4. The rate constants determined from the slopes of these plots are given in Table 4 and the plot of $\log k$ vs $1/T$ is shown in Figure 5. The least squares fit of the data yields the values for activation energy and frequency factor given in Table 4.

The reaction rate was not altered when the surface area was increased by a factor of >10 by addition to the cell of prefluorinated Monel turnings. This establishes that the reaction is homogeneous. The rate was not affected by addition of NO and I₂ scavengers, indicating an absence of a free radical chain reaction. The kinetic evidence, except for the extremely high frequency factor, favors a mechanism with unimolecular decomposition as the rate-controlling step. Normal frequency factors are in the range 10^{13} to 10^{14} sec⁻¹, although a few higher values have been reported.

Product distribution and the change in products with addition of I₂ scavenger indicate that the principal decomposition reaction is a homolytic split between the two rings to form cyclohexyl radicals. The main products are perfluoro-1,1-dimethylcyclopentane, perfluoromethylcyclohexane, perfluorocyclohexane, perfluoromethylcyclopentane, perfluoro-1-methylcyclopentene, and perfluorocyclopentene. No unsaturated C₇ or sat-

Figure 4. First-order plots for the thermal decomposition of perfluorobicyclohexyl ($C_{12}F_{22}$).

Table 4

Kinetic Data for Thermal Decomposition of Perfluorobicyclohexyl

Temperature, °C	k , $\text{sec}^{-1} \times 10^6$
350	1.51
360	4.71
370	9.95
377	16.1
385	40.4

Arrhenius activation energy = 73.3 ± 3.7 cal/mole

Frequency factor = $10^{20 \pm 3} \text{ sec}^{-1}$

urated C_5 compounds have been found. A reasonable mechanism for formation of products can be formulated with the help of evidence obtained by Tatlow and co-workers [*Tetrahedron* 20, 1381 (1964)] showing that perfluorocyclohexyl radicals formed at elevated temperature undergo considerable isomerization to perfluoromethylcyclopentyl radicals. Under their experimental conditions they felt that isomerization occurred mainly to the 2-methylcyclopentyl radical. However, under our conditions 1-methylcyclopentyl appears to be the principal radical; otherwise isomers such as perfluoro-1,2- and 1,3-dimethylcyclopentane would be formed, whereas we find only the 1,1-dimethylcyclopentane. Further evidence for this postulate is the formation of only the 1-methylcyclopentene without any of the 2-methyl or 3-methyl isomers.

The principal reactions for which we have evidence thus far are:

Formation of the saturated C_7 and unsaturated C_5 compounds [Eqs. (3) and (4)] involves transfer of a CF_3 group from a methylcyclopentyl radical followed by internal rearrangement to form perfluorocyclopentene. The saturated and unsaturated C_6 compounds arise from radical disproportionations [Eqs. (5) and (6)]. It is highly probable that radical combination reactions occur also. Evidence for this is formation in significant amounts of two products of molecular weight near that of the starting compound. These compounds have been purified in small amounts, but not yet in sufficient quantity for complete characterization.

RADICAL INTERMEDIATES

A systematic study of the structure of free radicals and of radical ions should give information of value in elucidating the kinetics of a wide variety of organic reactions, ranging from biological processes to industrial syntheses. As part of such a study we have prepared the radical anions of a number of diazole derivatives by treatment of the parent compound with alkali metals in aprotic solvents such as tetrahydrofuran, and observed their electronic absorption and electron spin resonance (esr) spectra. Such spectra of the perfluoro-2,1,3-benzoselenadiazole radical anion (PBSe) are

Figure 5. Arrhenius plot of first-order rate constants for the thermal decomposition of perfluorobicyclohexyl ($C_{12}F_{22}$).

Figure 6. Progress of sodium reduction of PBSe in tetrahydrofuran. 1 is absorption spectrum of starting material, 6 is radical. (ϵ in liter-mole $^{-1}$ -cm $^{-1}$.)

presented in Figures 6 and 7A. Analysis of the observed 39-line esr spectrum yields the following isotropic hyperfine splitting constants: $a_F = 3.56$ and 4.34 gauss for the two sets of two equivalent fluorine atoms at positions 5,6 and 4,7 respectively, and $a_N = 6.08$ gauss for the two equivalent nitrogen atoms. Computer simulated spectra employing the above values are shown in Figures 7B and

Figure 7. (A) Electron spin resonance spectrum of $(PBSe)^-$, K^+ in tetrahydrofuran; (B) computer simulated spectrum; (C) stick reconstruction of the spectrum.

7C. Results of a semiempirical self-consistent field molecular orbital (SCF-MO) study of the molecule and the isologs 2,1,3-benzoselenadiazole and 2,1,3-benzothiadiazole were assessed by comparison of calculated and experimental esr and electronic spectra of the radicals. Similar comparisons were made of the neutral species. It was concluded that a model that employs the p -orbitals of the heteroatom satisfactorily describes the pertinent experimental data. (Calculations were done in collaboration with R.H. Felton of MIT; esr with B.H. Bielski, Chemistry Dept., BNL.) The experimental and theoretical work is being extended to similar heterocyclic compounds (containing oxygen, sulfur, and selenium) of biological interest. The anion radical of 1,2,5-thiadiazole has been prepared by reduction in dimethoxyethane at $-78^\circ C$. The esr spectrum (Figure 8) consists of 15 lines with $a_N = 7.0$ and $a_H = 2.5$ gauss.

Figure 8. ESR spectrum of 1,2,5-thiadiazole anion radical in dimethoxyethane; potassium gegenion, -73°C .

The cation radical of perfluoronaphthalene was prepared by oxidation with SbF_5 in methylene chloride. Tentative assignments of splitting constants for the two sets of four equivalent fluorines are 12 and 4 gauss.

FLUOROCARBON REACTIONS

Reaction intermediates are not, of course, limited to radicals and ions. Another type is the valence isomer, typified by Dewar benzene. The role of such species in the reactions of fluorocarbons, particularly in the processes of radiolysis and photolysis, has been investigated. It is expected that the results will have a wider application than to fluorocarbons alone. The new compound perfluoro (Dewar xylene) I, was prepared by gas and liquid-phase photolysis of decafluoro-*o*-xylene. Its structure was determined by IR and NMR. (NMR spectra by K.E. Wilzbach and L. Kaplan, Argonne National Laboratory.)

The related compounds, perfluoro-Dewar benzene (II) and -Dewar toluene (III), were also prepared by liquid-phase photolysis. Although gas-phase

syntheses were known, photolysis in hydrocarbon solutions was reported to result in hydrogen abstraction from the solvent without isomerization [I. HALLER, *J. Chem. Phys.* **47**, 1117 (1967)]. I, II, and III were identified by GLC, IR, and mass spectra in the gas- and liquid-phase γ radiolyses of their respective aromatic compounds. Radiolysis of II results in hexafluorobenzene and a new compound (IV) of mass 186 that decomposes back to II and hexafluorobenzene (sometimes explosively). IV is conjectured to be hexafluoroprismane. The G -value for the destruction of II is >10 molecules/100 eV for doses of 10^7 rads. The following sequence is suggested:

The role of valence isomerization in radiation chemistry remains to be determined. The intriguing question arises whether it may not be considered as an "energy sink," i.e., a pathway for storing the energy from excited states and the recombination of radicals and ions in the form of relatively long-lived species. The isomers could in turn either revert back to the ground state, an explanation for the "protective effect" of aromatic systems, or undergo further reaction.

In connection with previous work on the radiolysis of perfluoronaphthalene and perfluorobenzene, these compounds were fluorinated under mild conditions with fluorine and also with xenon difluoride. Two products were isolated, which are also predominant products of the radiolyses: $\text{C}_{10}\text{F}_{10}$ and C_6F_8 , respectively. Each results from the addition of 2F to the starting material. Thermal fluorination is believed to proceed via atomic fluorine attack [J.M. TEDDER, *Advan. Fluorine Chem.* **2**, 105 (1961)]. These reactions are therefore consistent with the proposed radiolytic mechanism whereby atomic fluorine, continuously produced during irradiation, attacks the aromatic ring.

Graphite Chemistry

J. CLARKE, B. FOX, J. TVEEKREM, A. WOLKE

THE GRAPHITE-HYDROGEN REACTION

The reaction of graphite and hydrogen has been studied at temperatures $>3000^\circ\text{K}$ to determine mechanism and products. Such a study should throw light on the formation of graphite, and should help to predict the composition of the hydrocarbons formed, and the energy balance, when small particles of graphite or carbon are heated by collision with fission fragments or alpha particles in the presence of hydrogen; acetylene is a primary product in this reaction.

The rates of reaction of graphite and hydrogen for temperatures between 3000° and 3500°K and pressures between 0.01 and 0.50 atm were determined; short reaction times (0.05 to 0.10 sec) were necessary at the highest temperatures to prevent excessive filament loss.

At pressures >0.10 atm, the carbon lost from the filament was almost completely converted to gaseous hydrocarbons, but at lower pressures, varying amounts deposited on the wall of the reactor vessel. A summary of the product composition as a function of pressure at 3500°K is shown in Figure 9. At all pressures, C_2H_2 is the primary product (79 to 99%). C_2H_4 is an important product at $P(\text{H}_2) > 0.05$ atm and increases to 17% at 0.5 atm. The only other hydrocarbons formed are small amounts of CH_4 and C_2H_6 , which are probably formed at temperatures

$<3000^\circ\text{K}$ during the heating and cooling of the filament.

Earlier work had indicated that the reaction of graphite and hydrogen above 3200°K involves the vaporization of graphite to C_1 , C_2 , and C_3 species and the reaction of these with hydrogen in the vapor phase. Our own spectroscopic observations and heat balance measurements of the heat of vaporization of graphite filaments show that C_2 is probably the most important if not the only carbon species vaporizing from graphite.

In Figure 9 it is seen that at 3500°K , as the pressure of H_2 is reduced, the percent C_2H_2 in the product increases and at 0.01 atm is $>99\%$. This also indicates that only C_2 is vaporized from the graphite and these molecules add to H_2 to form C_2H_2 . The absence of significant amounts of CH_4 or C_3H_8 indicates the absence of C_1 and C_3 in the vaporized species. The increase in C_2H_4 as the hydrogen pressure is increased would be accounted for by the addition of H_2 to activated C_2H_2 . Mass spectrometric analysis of the hydrocarbon product at 0.01 atm and at 3500°K where an excess of graphite was vaporized showed that C_4H_2 and C_4H_4 were formed, but insignificant amounts of odd-numbered carbon compounds. This also indicates the absence of odd-numbered carbon species in the vaporization of graphite. C_4H_2 would result from the addition of C_2 to activated C_2H_2 . A study of the temperature gradient around filaments shows that the temperature drops off rapidly with distance from the filament, and thus most of the collisions between carbon species and hydrogen would be at temperatures considerably below the filament temperature.

An apparatus was constructed to measure the gas temperature profile around a heated filament so that the reaction variables could be determined. It consisted of a heated filament in a bell jar enclosure with a platinum resistance gas thermometer which could be positioned at measured distances from the heated filament. With this apparatus, the thermal conductivity of helium was measured as a function of temperature and pressure and was shown to agree with the literature values. The Langmuir film thickness was measured directly and shown to vary inversely as the square root of the pressure; it varied from 7.0 mm at 1 atm to >60 mm at 0.01 atm. Since the film thickness gives the distance through which heat is transported by conduction rather than convection, it is seen that in the filament reactor (radius, 20

Figure 9. Effect of pressure on product composition in the reaction of carbon and hydrogen at 3500°K .

mm) at high pressure the section near the walls was at room temperature, while at low pressure it was significantly above room temperature. There may be a small region near the filament where the temperature is essentially constant and significantly lower than that of the filament. This is being investigated.

Work on the reaction of carbon and hydrogen at <1 atm is continuing. In addition, a reactor has been constructed to measure the reaction rates at pressures up to 10 atm; a knowledge of these rates should be of value to the nuclear rocket engine program.

SPECTROSCOPIC STUDY OF CARBON-HYDROGEN SYSTEM

Spectral studies of carbon vapor species, and intermediates in carbon-gas reactions, comprise an integral part of the graphite chemistry program. Observations were made on thin-walled graphite tubes which were resistively heated with direct current to temperatures as high as 3400°K for times of 0.5 to 10 sec at power levels of 3 to 5 kW. The temperature of the outside of the tube was monitored with a photoelectric pyrometer and generally remained constant during the last 80% of each run. This temperature was corrected by an amount proportional to the input power and thermal conductivity of graphite to obtain the temperature inside the tube. The correction generally amounted to 100° to 200°K at the power levels employed. A four-trace storage oscilloscope was employed to monitor the current, voltage, temperature, and photomultiplier tube signal with respect to time during the experiments.

The emission intensity of the C_2 bandhead at $5165\text{ \AA}$ was monitored photoelectrically as a function of temperature in 0.1 atm of helium. The continuous radiation from the wall of the hot graphite tube was corrected for by making identical runs at $5170\text{ \AA}$ where no C_2 radiation occurred. Treatment of the emission intensity data by the second law of thermodynamics yielded a heat of sublimation of C_2 in the excited state at 3000°K of 258 kcal/mole. After correction for the heat content and excitation energy, a heat of sublimation of C_2 in the $^1\Sigma_g^+$ ground state at 0°K of 214.5 kcal/mole was obtained. This agreed exactly with the value obtained from the convergence limit of the $^1\Pi_u$ state of C_2 but was 10% higher than the currently accepted value of 195 kcal/mole. The

value of 195 kcal/mole is based on several 2nd and 3rd law measurements employing both mass and optical spectroscopy.

Initial experiments to measure the pressure of C_2 by absorption spectroscopy were carried out in 0.1 atm of helium. The values obtained at 3200° to 3300°K appeared to be approximately one order of magnitude lower than the calculated equilibrium pressures. These absorption measurements will be extended to hydrogen atmospheres where it would be expected that the C_2 pressure at a specified temperature would be lower because of the predicted presence of species such as C_2H and CH in addition to C_2H_2 . A comparison of the C_2 emission intensity in hydrogen and helium showed a twofold decrease in hydrogen.

C_3 has not been detected, although other investigators have found a higher equilibrium pressure for this molecule than for C_2 . Thus our data indicate an upper limit of the C_3 pressure at least a hundred times less than the thermodynamically calculated value. The literature reveals two cases by other investigators who have also been unable to detect C_3 . In one case, graphite was heated in vacuum by a laser and in the other, ethylene was being pyrolyzed in a shock tube. The most probable explanation would appear to be a nonequilibrium situation in one or the other set of experiments; in which one, we cannot yet say.

Metal Hydrides

J. REILLY, R.H. WISWALL, JR.

Hydrogen will react directly and reversibly with many metals and alloys to form metal hydrides. Such reversible hydrides may prove useful as a convenient and cheap means to store hydrogen which is ultimately evolved and used as a fuel. However, while the reaction of H_2 with single metals has been extensively investigated, only a relatively modest amount of work has been concerned with the interaction of H_2 with metal alloys. Further, no systematic work has been carried out with alloy systems that may require relatively high pressures to form reversible hydrides even though it is these systems which appear to be particularly promising for the storage of hydrogen. Thus it is to these latter systems we have addressed ourselves.

A number of alloys have been investigated, the most promising of which are the Mg-Cu alloys and

Figure 10. Uptake of hydrogen by Mg_2Cu ; pressure vs composition.

Figure 11. Uptake of hydrogen by $\text{Mg}_2\text{Cu} + \text{Mg}$; pressure vs composition.

Mg-Ni alloys discussed below. A description of the experimental equipment and procedure has been given previously [BNL 50023 (S-69)].

MAGNESIUM-COPPER ALLOYS

Magnesium forms two intermetallic compounds with Cu: Mg_2Cu and MgCu_2 . The latter did not react with H_2 at temperatures up to 350°C and H_2 pressures of 330 psia; however, Mg_2Cu reacted fairly rapidly at 300°C and H_2 pressures of ≈ 300 psia.

In Figure 10 are shown several pressure-composition isotherms for the $\text{Mg}_2\text{Cu-H}_2$ system. As usual with such isotherms, there is an ascending curve on the left where a solid solution of hydrogen in the metal phase (Mg_2Cu in this case) exists. This is followed by a pressure plateau. It is believed that its appearance corresponds to the initiation of the reaction

where all the solid phases are understood to be saturated with hydrogen. When the hydride was decomposed by removing H_2 , an x-ray diffraction pattern of the residue showed only the phase Mg_2Cu to be present, which was the initial starting material; thus reaction (1) is reversible.

To the right of the plateau, the isotherm probably ascends very steeply because of the fact that MgH_2 is almost a stoichiometric compound and the dissolution of hydrogen in MgCu_2 is negligible. This portion of the isotherm is represented as a dashed line and could not be definitely established because a small amount of solid hydride had to be decomposed before the first equilibrium point on the right could be defined. A plot of the dissociation pressures in the plateau region vs the reciprocal of the absolute temperature gave a straight line which obeyed the relationship $\log P_{\text{atm}} = -(A/T) + B$, where $A = 3089$ and $B = 7.437$. Thermodynamic functions per mole of H_2 for reaction (1) calculated from these data are given below.

$$\Delta H_{298}^0 = -17.4 \pm 1.0 \text{ kcal/mole of } \text{H}_2,$$

$$\Delta F_{298}^0 = -7.3 \pm 1.0 \text{ kcal/mole of } \text{H}_2,$$

$$\Delta S_{298}^0 = 34.0 \pm 0.7 \text{ eu/mole of } \text{H}_2.$$

If Mg is present in the alloy in excess of the composition corresponding to Mg_2Cu , the pressure composition isotherm exhibits two plateaus as shown in Figure 11. In this case it is believed that the lower pressure plateau is due to the known reaction of Mg with H_2 :

When all the free Mg is exhausted, the second and higher plateau appears, which is due to reaction (1) of the intermetallic compound Mg_2Cu with H_2 . In these alloys the lengths of each pressure plateau are proportional to the relative amounts of free Mg and Mg_2Cu initially present. The arrows shown in Figure 11 mark where the boundary between the upper and lower plateaus should occur as predicted by reactions (1) and (2). The calculations did not take into account the formation of solid solutions which occurs to some extent as indicated by slope of the line connecting the two plateaus.

It is interesting to note that the presence of Mg_2Cu apparently has a catalytic effect for reaction (2), since substantially higher H_2 pressures and temperatures are necessary to form MgH_2 from Mg alone.

A plot of the dissociation pressure of MgH_2 in the presence of Mg_2Cu vs the reciprocal of the absolute temperature yields a straight line obeying the relationship $\log P_{\text{atm}} = -(4094/T) + 7.299$. The thermodynamic functions for the formation of MgH_2 calculated from these data, assuming Mg_2Cu acts purely as a catalyst, are:

$$\begin{aligned} \Delta H^0_{f298} &= -18.7 \pm 1.0 \text{ kcal/mole,} \\ \Delta F^0_{f298} &= -8.7 \pm 1.0 \text{ kcal/mole,} \\ \Delta S^0_{f298} &= -33.4 \pm 0.7 \text{ eu/mole.} \end{aligned}$$

MAGNESIUM-NICKEL ALLOYS

The Mg-Ni system is quite similar to the Mg-Cu system. Two intermetallic compounds are formed, Mg_2Ni and MgNi_2 , of which only Mg_2Ni reacts with H_2 . However, the product of this reaction has a hitherto unknown x-ray diffraction pattern quite different from that of the starting phase, Mg_2Ni , and without any evidence of the presence of MgNi_2 . Thus, it has been assumed to be a new ternary hydride and based on stoichiometric considerations the following equation has been tentatively adopted:

In any case the reaction is reversible, since the initial starting material is regenerated upon decomposition of the hydride. Figure 12 shows several pressure composition isotherms for the Mg_2Ni - H_2 system. As shown in Figure 13, in the presence of excess Mg, two plateaus are formed. The lower

Figure 12. Uptake of hydrogen by Mg_2Ni ; pressure vs composition.

Figure 13. Uptake of hydrogen by $\text{Mg}_2\text{Ni} + \text{Mg}$; pressure vs composition.

plateau is attributed to the formation of MgH_2 (reaction 2). The upper plateau, due to reaction 3, appears when all the free Mg is exhausted. As with Mg_2Cu , the presence of Mg_2Ni has a strong catalytic effect on the reaction between Mg and H_2 .

A plot of the dissociation pressure of Mg_2NiH_4 vs $1/T$ yielded a straight line obeying the relationship $\log P_{\text{atm}} = -(3360/T) + 6.389$ from which the following thermodynamic quantities were calculated:

$$\Delta H_{f298}^0(\text{Mg}_2\text{NiH}_4) = -30.7 \pm 2.0 \text{ kcal/mole,}$$

$$\Delta S_{f298}^0(\text{Mg}_2\text{NiH}_4) = -58.4 \pm 3.0 \text{ eu/mole,}$$

$$\Delta F_{f298}^0(\text{Mg}_2\text{NiH}_4) = -13.4 \pm 2.0 \text{ kcal/mole.}$$

Preliminary experiments on the rate of decomposition of Mg_2NiH_4 have indicated that it is a first-order reaction with $k \cong 1.4 \times 10^{-2} \text{ sec}^{-1}$ at 240°C . A decomposition rate of this order should insure an adequate supply of H_2 to practical devices such as fuel cells or combustion engines, the waste heat of which could supply the enthalpy of decomposition.

OTHER ALLOYS

In Table 5 are given the results of screening various alloys for hydride formation. The procedure with a new alloy was slightly different from that described for the Mg-Cu and Mg-Ni alloys. In this case the alloy was ground to -25 mesh in a dry box and transferred under an inert solvent (acetone or methyl pentane) to the experimental rack. The solvent was evaporated and the sample heated to $\approx 325^\circ\text{C}$ and outgassed for 1 hr. The sample was then exposed to H_2 at $\approx 350 \text{ psia}$ at a temperature of 300° to 350°C . After several hours the H_2 was removed and the sample outgassed, after which the entire cycle was repeated at least twice. If no H_2 absorption took place in this temperature range, the sample, still under H_2 pressure, was cooled slowly overnight to room temperature. The amount of H_2 absorbed, if any, was determined by the drop in reservoir pressure and/or by combustion analysis of the sample.

Electrode Kinetics

S. JAMES

The work on the $\text{Ti(I)}\text{-Ti(III)}$ electrode in acidic media was completed and the results were pub-

Table 5
Hydrogen Uptake by Alloys

Alloy composition, wt %	Probable starting phase	Max hydrogen content, wt %
60 Cd, 40 Mg	Mg_3Cd	0.42
40 Ca, 60 Sn	Ca_2Sn	0.53
38 Ca, 62 Zn	CaZn	1.77
60 Ti, 40 Cu	Ti_2Cu	2.32
60 Mg, 40 Cr	-	<0.1
40 Mg, 60 Al	$\beta + \gamma$	0.78
35 Mg, 65 Al	$\gamma + \beta$	<0.1
41 Mg, 59 Al	$\beta + \gamma$	0.67
77 Mg, 8 Cu, 14 Li	-	2.0
70 Cu, 30 Al	η_2	<0.1
60 Al, 40 Ni	NiAl_3	<0.1
56 Al, 44 Co	Co_2Al_5	<0.1
57 Mg, 40 Al, 3 Ni	-	1.53
10 Li, 90 Zn	LiZn	0.24
67 Mg, 33 Si	Mg_2Si , Mg	0.33
76 Mg, 22 Co	$\text{Mg} (+ \text{Mg}_2\text{Co}?)$	5.33
75 Mg, 25 B	MgB_2	1.16
37 Al, 63 Ti	TiAl	0.20
46 Mg, 54 Co	$\text{Mg}_2\text{Co}?$	2.1

lished [*Electrochim. Acta* **12**, 939-54 (1967)]. Observations made during this research suggested that certain current ideas on the effect of electrochemical activation on platinum electrodes were wrong, and a brief investigation of this topic was undertaken.

It is well known that smooth platinum electrodes are activated by alternate electrical oxidation and reduction treatments; that is, for a given electrode reaction, a higher current density can be obtained at a given impressed voltage after the activation than before. The activation is not permanent but decays at rates that depend on the activation procedure and on the postactivation conditions. The reason for the activation has been attributed (a) to desorption of adsorbed contaminants, (b) to a change in the nature of the surface layers of the platinum (the "platinization" theory), and (c) to the partial oxidation of the outermost layer, producing a state of high electrocatalytic activity. To help distinguish among these, the effect of oxidation-reduction treatments was determined on platinum in electrolytes of ordinary reagent-grade purity, and again in a parallel series of experiments in which extraordinary precautions were taken to remove all traces of adsorbable impurities. The method involved percolating the solutions through a column of specially purified activated charcoal; details will be found in the

Figure 14. Effect of alternate anodization and cathodization (A-C) on anodic currents at a Pt RDE. Rpm, 1500; applied voltage, 30 mV; electrolyte, 1 M HClO₄, 0.0106 M in Fe(II) and Fe(III). Curves A and B: before and after A-C in purified solution. Curves A' and B': before and after A-C in unpurified solution.

published article mentioned above. The reaction used to test the electrode activity was the oxidation of Fe(II). The platinum was in the form of a rotating disk, as in the thallium research.

The results are shown in Figure 14, which gives the change in current with the passage of time for electrodes before and after activation in purified and unpurified solutions. It can be seen that the effect of activation is about the same as that of using purified solution, and that in the unpurified solution the effect of activation rapidly decays. These experiments clearly provide strong support for the theory that activation consists of the removal of absorbed contaminants.

It is to be noted that another type of activation probably results when the oxidation-reduction is repeated scores or hundreds of times. The behavior, as described in the literature, of platinum electrodes which have been so treated is consistent with a modification of the metal structure to a depth of several atomic layers. A contribution of the present work is to establish a distinction between two types of activation.

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Radiation Division

B. MANOWITZ

Radiation Research

D. METZ

SOLID-STATE REACTIONS

Preirradiated crystals of propionamide, *n*-butyramide, and isobutyramide absorb relatively large quantities of oxygen. In propionamide and *n*-butyramide, the chief products are hydroperoxide and α -ketoamide, which account for 60% and 10 to 30%, respectively, of the oxygen absorbed. In isobutyramide, the principal product is a hydroperoxide (accounting for 95% of the absorbed oxygen) formed in yields as high as 8% by a chain oxidation with a kinetic length of much more than 100. In addition to the hydroperoxide, which appears to nucleate as a separate phase, a small amount of unidentified acid is also formed. The yields of hydrogen peroxide and alkyl peroxide appear to be negligible.

X-ray diffraction studies show that the reaction with oxygen is accompanied by a marked expansion of the lattice in the $\langle 100 \rangle$ direction. The relative rates of radical quenching by oxygen in volume (γ -ray) and surface- (Tessla coil) irradiated crystals and direct determination of peroxide yields from different parts of a large single crystal are all consistent with the view that the oxygen enters into the crystal lattice and diffuses more readily between certain layers of the lattice. This is further confirmed by the kinetics of oxygen absorption by large irradiated single crystals.

It has also been observed that other gaseous reactants, such as NO, SO₂ and ethylene, can react with irradiated linear crystalline amides. In the case of NO, initially about three molecules are absorbed per radical. Subsequent evacuation leads to the formation of a new radical with a spectrum similar to that obtained through irradiation of an oxime. Readmission of NO results in an increased rate of radical decay, indicative of an expansion of the crystal lattice caused by the previous adsorption of NO.

Absorption of SO₂ leads to the formation of a long-lived sulfinic radical. Absorption of ethylene results in a chain reaction, whose end product has not been identified.

G. ADLER, A. FAUCITANO,
A. PEROTTI, W. REAMS

RADIOLYSIS OF AROMATIC COMPOUNDS

In an attempt to understand the origin of the large nitrogen yield from irradiated *m*-tolunitrile and to check the hypothesis of the formation of an intermediate azo compound, both benzonitrile and acetonitrile were studied. The former compound was found to be too radiation resistant, with very little decomposition occurring at doses of 5×10^7 rads. The product analysis of irradiated acetonitrile is shown in Table 1. From these data it is obvious that nitrogen is not formed through the dimerization to an azo compound followed by decomposition. The composition of the "polymer" was found to be 5.8% H, 59.9% C, and 34.9% N, which corresponds to the empirical formula (C₂H₂N)_n and indicates that it might be pyrazine.

These studies have not elucidated the mechanism of nitrogen formation from tolunitrile.

J. WEISS, A. NISHIHARA, N. CARCIELLO

Table 1
Radiolytic Yields From Acetonitrile^a

Compound	G-value
Hydrogen	0.58
Methane	0.62
Ethane	0.026
Ethylene	0.014
Acetylene	0.029
Propane	0.002
Nitrogen	0.009
Succinonitrile	0.55
β -Amino crotonitrile	0.16
Propionitrile	0.25
Polymer	7.33

^aDose range: 5×10^6 to 5×10^7 rads at 60°C.

VINYL POLYMERIZATION MECHANISMS

The temperature behavior of the polymerization rate of both styrene and α -methylstyrene using γ -ray initiation and under conditions such that the ionic processes are predominant has been investigated. For styrene, this behavior is quite complicated, as is shown in Figure 1, a schematic representation of the data. It is immediately obvious that the data cannot be interpreted in terms of a simple, one-ion propagation reaction mechanism.

For α -methylstyrene, although the isotherms do not cross, other anomalies appear which cannot yet be rationalized on the basis of a simple mechanism. These temperature effects are being more intensely studied.

Over the same temperature and dose-rate ranges shown in Figure 1, subtle but real changes in average molecular weights occur. Fractionated samples are now being studied by vapor fractometry.

D. METZ, A. GLINES, C. JOHNSON, R. POTTER

RADIOLYSIS IN THE ADSORBED STATE

The radiolysis of nitrous oxide adsorbed on silica gel and Linde 13 $\times$ molecular sieve is being studied. Surface areas of the solids were determined by the gas adsorption method with the use of nitro-

Figure 1. Radiation-induced ionic polymerization of styrene at several temperatures.

Table 2

N_2O on Silica Gel
(Outgassed 450°; surface coverage $\theta=0.025$;
total dose = 9.1×10^5 rads.)

Dose rate, rads/hr	$G_T(N_2)$
6.4×10^3	2.5
7.3×10^3	2.4
2.60×10^4	2.7
3.22×10^4	2.5
6.60×10^4	2.4
1.69×10^5	2.5
2.40×10^5	2.3
9.80×10^5	2.7
	2.5 ± 0.1

gen. Analysis of the adsorption isotherms of N_2O at several temperatures leads to the conclusion that this gas is physically adsorbed on the surface of both sides.

In both these solids the observed $G(N_2)$ values are so high that efficient energy transfer from solid to adsorbed N_2O must be invoked. A mechanism has been proposed in which electrons from the bulk solid rapidly migrate to the surface, where they either react with N_2O to yield N_2 and O^- or they become trapped. Both O^- and trapped electrons then react with "holes." On the basis of this mechanism it can be predicted that $1/G(N_2)$ should be a linear function of the reciprocal of the surface concentration of N_2O , and $G(N_2)$ should be independent of the dose rate. The first prediction is fitted by the experimental data over the surface concentration range of 0.01 to 0.20 (for N_2O on silica gel); these data yield a value of $G(e^-) = 3.7$. The second prediction is borne out by the data shown in Table 2.

The data available from the experiments using molecular sieves also appear to fit this mechanism.

Previously reported work on the radiolysis of CO_2 in the adsorbed state has been accepted for publication. R. GOODRICH, J. SUTHERLAND

RADIOLYSIS OF LIQUID AMMONIA

The radiolyses of solutions of pure hydrogen, pure hydrazine, and mixtures of hydrogen and hydrazine in liquid ammonia have been studied. A serious difficulty with the method of analysis for hydrazine has been traced to impurities in a batch of hydrochloric acid. R. GOODRICH, J. SUTHERLAND

CRITICAL POINT RADIOLYSIS

The yields of nitrogen and oxygen from nitrous oxide irradiated in glass vessels are being investigated as a function of gas density at 38°C ($T_c = 36.5^\circ\text{C}$). These results are being compared with those of experiments performed in the liquid and solid states at 10°, -78°, and -196°C. Preliminary results indicate that the nitrogen-to-oxygen ratio remains fairly constant in the density range 0.002 to 0.70 g/cc, and also into the liquid and solid states. Detailed analysis requires more accurate dosimetric data, and methods for obtaining such data are being investigated. J. SEARS, J. SUCHER

NITROGEN CHEMICAL PHYSICS

The luminescence induced in nitrogen by the deposition of fission fragment energy (Cf^{252}) as a function of track length was measured by a photomultiplier pulse-height technique. The amount of formation per unit track length of the emitting molecular species ($C^3\Pi_u$) was calculated, the process being $\text{N}_2(C^3\Pi_u) \rightarrow \text{N}_2(B^3\Pi_g) + h\nu$. The efficiency of formation of this luminescent state was found to remain practically constant to the very end of the fission fragment track. Toward the end of the track, nuclear elastic collisions (NEC) became the dominant mode of energy deposition rather than coulombic interactions. Secondary electrons are probably responsible for the formation of the $C^3\Pi_u$ state. Zeroth-order NEC cannot account for the excitation at the end of the track; therefore a more detailed theory than now exists must be formulated. J. SEARS, R. RODGERS

OZONE SYNTHESIS

The investigation of the γ radiolysis of oxygen has been completed, and the detailed results have been submitted for publication. The fission fragment irradiation data on oxygen are also being submitted for publication. J. SEARS, J. SUTHERLAND

Radiation Chemical Processing Program

M. STEINBERG

This program is concerned with performing experimental and design studies on the application

of isotopic radiation energy for chemical processing, generally for high G -value, chain-type reactions. Survey and detailed studies are carried out on a broad technical basis to develop process principles and to search for economically promising systems.

ETHYLENE HOMOPOLYMERIZATION

The study of the radiation-induced polymerization of ethylene is being carried out at a reduced rate because of the considerable amount of industrial research effort that has been generated by the BNL program. Before completing this program, an attempt is being made to operate a small-scale flow experiment. The purpose of the experiment is to obtain sufficient quantities of polymer from a flow system for product characterization and to determine the operating characteristics of a radiation-induced high-pressure process.

In the flow experiment a 420-cc volume reaction vessel was used. The lower portion of the vessel was shielded to prevent postirradiation of any polymer that was held up in the vessel. The experiment was carried out at a reaction temperature of 200°C and a radiation intensity of 1.3×10^5 rads/hr. Three operating pressures, 405, 690, and 850 atm, were investigated. A total of 605 g of polyethylene was collected. The polymerization rate, based on the volume of the vessel, was considerably lower than that predicted from the rate equation derived from earlier capsule experiments. In this equation, the rate is based on the gas volume in the vessel. On completion of the experiment, the reaction vessel was disassembled and inspected and was found to be completely filled with polymer (≈ 300 g). The polymerization rate based on the gas volume was therefore much greater

Table 3

Properties of Radiation-Produced Polyethylene

Radiation conditions	200°C, 850 atm	200°C, 680 atm
Density	0.910 g/cc	0.905 g/c
Melt index	0.006 g/10 min	0.001 g/10 min
Melting point	71° and 95°C	69° and 92°C
Crystallization	63° and 94°C	63° and 89°C
Solubility	100% soluble in <i>o</i> -dichlorobenzene at 135°C	100% soluble in <i>o</i> -dichlorobenzene at 135°C
Film properties	clear pliable film	clear pliable film

than that originally estimated. Comparison with the rate equation is not possible because of the uncertainty of the gas volume in the radiation field for the duration of the experiment.

The polyethylene formed during the experiment was divided into batches that were thought to represent operating conditions of 680 and 850 atm at 200°C.

The polymers were ground to uniform-size pellets and evaluated for density, melting point, melt index, solubility, and film-forming characteristics. Table 3 gives the over-all results.

The melting point curves of both polymers showed a very broad melting range, with maxima at points specified in Table 3. Upon recrystallization, two peaks were evident, which is generally common for a physical mixture of two polymers. From the melting point and crystallization curves, it can be said that the polyethylenes formed were very heterogeneous and appeared to be a blend of two or more polyethylenes.

An experiment designed to operate in a single-phase region was started in an attempt to reduce the problem of plugging in the reaction vessel. Operating conditions selected were 1200 atm, 200°C, and a radiation intensity of 2.3×10^5 rads/hr. The system had been operating for 15 min when a decomposition occurred which resulted in the failure of a burst disk. The system has been cleaned and reassembled. Modifications have been made in order to give a more accurate temperature measurement and to facilitate the clean-up of the system in the event of further decompositions.

The construction of an addition to the High Pressure Laboratory has been taking place throughout the last half of the year, and as a result the re-starting of the flow system has been delayed.

L. KUKACKA, P. COLOMBO, J. FONTANA,
J. VARELA, K. KANIGE

ETHYLENE COPOLYMERIZATION

Ethylene-SO₂ Copolymerization

A problem encountered during the study of the ethylene-SO₂ copolymerization reaction was the solubility of ethylene gas in liquid SO₂. In a two-component system consisting of a gas and a liquid, the composition of the mixture depends on the solubility of the gas in the liquid at various temperatures and pressures. Because of the lack of available solubility data on this system, several ex-

Table 4
Solubility Data for Ethylene Gas in Liquid SO₂

Temperature, °C	Total pressure, atm	Partial pressure, atm		Ethylene soluble in SO ₂ (wt %)
		Ethylene	SO ₂ ^b	
20 ^a	340.0	336.9	3.1	5.28
40	432.0	425.9	6.1	6.50
60	512.2	501.3	10.9	7.95
80	559.3	542.3	17.0	9.42
100	689.8	663.3	26.5	11.38

^aInitial charge conditions at 20°C determined gravimetrically.

^bVapor pressure of SO₂ gas.

periments were conducted to determine the ethylene concentration in the liquid mixture for a range of conditions used in this work. Table 4 shows the concentration of ethylene in the mixture and the pressure increase as a function of temperature. A reaction vessel of known volume was charged with a measured amount of liquid SO₂; it was then pressurized with ethylene gas at 20°C. The temperature in the sealed vessel was increased to 100°C in increments of 20°C, and equilibrium pressures were noted at each temperature. The amount of ethylene soluble in SO₂ was calculated from the total mass and from ethylene data obtained under the same conditions of pressure and temperature. Corrections were made for the partial pressure of SO₂ and for the volume expansion of the liquid over the temperature range used.

Melt transition temperatures for ethylene-SO₂ copolymers formed by γ radiation in the gas and liquid phases are shown in Figure 2. Over the range of copolymer SO₂ concentration from 9 to 31 mole %, the melting points were essentially the same at 126° to 128°C. These values fall in the same range as those obtained for pure polyethylene formed under the same conditions of temperature, pressure, and radiation intensity. Melt transitions could not be detected for copolymer containing >44 mole % SO₂ at temperatures up to the decomposition point.

To determine whether the copolymers were crystalline at SO₂ concentrations >44 mole %, x-ray diffraction traces were made for copolymer containing 9 to 50 mole % SO₂. The traces shown in Figure 3 indicate the presence of crystalline material over the range of concentrations used.

Figure 2. Melting thermograms of ethylene polysulfones. Copolymer containing (a) 9 mole % SO_2 , (b) 20 mole % SO_2 , and (c) 31 mole % SO_2 .

Figure 3. X-ray diffraction scans of ethylene- SO_2 copolymers. (a) Pure polyethylene, (b) 9 mole % SO_2 , (c) 21 mole % SO_2 , (d) 31 mole % SO_2 , (e) 44 mole % SO_2 , (f) 50 mole % SO_2 .

However, as the SO_2 content increases, the amount of crystallinity apparently decreases. The crystal patterns, particularly for the lower SO_2 concentrations, closely resemble that for polyethylene. At 9% SO_2 , reflections are obtained that are due to both the orthorhombic and triclinic forms of polyethylene. The pattern is very similar to that for polyethylene (Figure 3a) formed by radiation polymerization under the same conditions. The ratio between the triclinic and orthorhombic forms increases with increasing SO_2 in the copolymer. Between 31 and 44% SO_2 the orthorhombic form can no longer be detected. Apparently the triclinic form can accommodate the SO_2 more easily than the orthorhombic, since this form persists. The disruption due to the SO_2 affects the size, quantity, and perfection of the crystallites, as indicated by the line broadening and the increase in amorphous content. Since the copolymers are crystalline even in the range where no melt transition temperatures were observed, it appears that the melting points for copolymer containing >31 mole % SO_2 are at or higher than the decomposition temperatures.

Ethylene-Vinyl Chloride Copolymerization

The Co^{60} γ -ray-initiated copolymerization reaction between ethylene and vinyl chloride is under investigation. The objectives of this work are (1) to study the kinetic behavior of this system, (2) to incorporate small amounts of vinyl chloride into the ethylene chain for improving the processability of γ -ray-initiated polyethylene, and (3) to incorporate small amounts of ethylene into vinyl chloride chains to act as an "internal" plasticizer for improving the processability and the flexible properties of vinyl chloride.

Initial experiments have been performed at 20°C with use of gas mixtures of ethylene and vinyl chloride. At total pressures of 340 atm, the maximum concentration of vinyl chloride in the gas mixture, due to its partial pressure at 20°C , is 11.4 mole %. The product obtained under these conditions, at conversions of 2 to 5%, was in the form of a fine white powder. Elemental analysis of the copolymers showed a vinyl chloride concentration of 3.5 mole %. These copolymers were easily pressed into clear, pliable film on a Carver Press at 150°C . Melting points ranged between 105° and 110°C , as compared with a melting point of 124°C for pure polyethylene formed under the

same conditions of pressure and temperature. Complete solubility was obtained in dichlorobenzene at 100°C. To increase the initial concentration of vinyl chloride in the gas mixture, higher reaction temperatures are necessary. A jacketed reaction vessel has been built capable of controlling reactor temperatures from 0° to 200°C. Other equipment for continuous pressure and temperature recordings is being assembled. Following the gas-phase work, the gas-liquid monomer system will be studied.

P. COLOMBO, J. FONTANA

COMPOSITE MATERIALS

Concrete-Polymer Materials

A cooperative program has been established with the Bureau of Reclamation, U.S. Department of the Interior, to study the formation of concrete-polymer combinations by the γ -radiation- and chemical-initiated polymerization of monomers impregnated in concrete. The purpose of the program is to attempt to improve the resistance of concrete to corrosion by distilled water, hot brine, and high sulfate brines in connection with the use of concrete as a material of construction for flash distillation units in water desalination plants. Improvements in strength, in resistance to cavitation due to fluid dynamic inconsistencies, and in resistance to spallation due to freezing and thawing conditions are also desired. The program includes the *in situ* polymerization of monomers in concrete, and the addition of monomers to wet concrete with the polymerization being initiated prior to and after setting.

The evaluation of a series of 1 × 1 × 8.5-in. mortar test specimens using styrene and methyl methacrylate was completed by the Bureau of Reclamation. Petrographic examination of the samples indicated a thorough impregnation with polymer.

The compressive strength of the impregnated bars was increased 2 to 2.4 times, styrene giving the greatest increase. Absorption of water was decreased from 80 to 98%. Hardness increased 1.4 and 1.9 times for styrene- and methyl methacrylate-impregnated bars, respectively.

A series of preformed concrete test specimens was prepared and forwarded to the Bureau of Reclamation for evaluation. Monomers under test are methyl methacrylate, styrene, and a mixture containing 60 wt % styrene-40% acrylonitrile. Testing of these materials is under way. Initial results indicate improvement in the following properties: tensile strength, compressive strength, resistance to abrasion, water absorption, resistance to freeze-thaw attack, corrosion resistance to distilled water, and resistance to forces of cavitation.

Experiments are being carried out to study the feasibility of adding monomers to wet concrete. Monomers being studied are methyl methacrylate, styrene, acrylonitrile, and a mixture of styrene-divinylbenzene. Polymerization was initiated prior to and after setting. Evaluation of these samples is under way. Measurements of the compressive strength and water absorption indicate improvements in both properties.

L. KUKACKA, P. COLOMBO, J. FONTANA,
J. VARELA, K. KANIGE

Sand-Plastic Composite

Mixtures of silica sand and methyl methacrylate (MMA) monomer were polymerized in the form of solid cylindrical rods and in the form of pipe. The samples contained ≈ 18 to 20% methyl methacrylate by weight. Polymerization was initiated with Co^{60} γ radiation at 20°C and with benzoyl peroxide at an oven temperature of 55°C. A specimen formed by each method was tested for compressive and tensile strengths, and the results obtained are given in Table 5.

Table 5

Compressive and Tensile Strength Tests

Specimen No.	Monomer used	Method of polymerization	Compressive strength, psi	Tensile strength, ^a psi
M-5660	MMA	Benzoyl peroxide	10,216	713
M-5661	MMA	γ -Rays	10,980	968

^aSpecimens were partially broken in flexure, which resulted in lower strength values than would be expected from tension above.

The strength values are considerably higher than those normally obtained for ordinary concrete. Attempts will be made to determine the effect of polymer concentration on strength and other properties. Addition of glass wool, asbestos, and other fillers is also being considered.

P. COLOMBO, J. FONTANA, G. FARBER

Fly Ash-Plastic Composite

A mixture of fly ash and methyl methacrylate monomer (50% by wt) was polymerized by Co^{60} γ radiation in the form of a solid cylindrical rod $\frac{1}{2}$ in. in diam by 6 in. long. The rod was cut into $\frac{1}{2}$ -in. lengths for compressive strength tests. Although the samples contained many air pockets, compressive strength values were obtained which varied from 7500 to 9600 psi. More uniform sample preparations should yield higher values than those obtained previously. Larger samples are being prepared for more extensive tests.

P. COLOMBO, J. FONTANA

HETEROGENEOUS RADIATION CHEMISTRY

NH_3 Synthesis

In concluding the study of the iron-catalyzed synthesis of ammonia from N_2 and H_2 at pressures from 3 to 171 atm, temperatures from 250° to 525°C, and flows from 3000 to 20,000 cc/hr, several experiments were performed with γ radiation from Co^{60} at an intensity of 4.4 megarads/hr.

A definite negative effect of irradiation has been shown to occur for both the pure synthesis gas (75% H_2 -25% N_2) and that containing 105 ppm O_2 . For both gases there appears to be about a 10% decrease in the ammonia yields between 400° and 500°C when compared with the data obtained without radiation. This percentage decrease becomes more significant at lower temperatures with the O_2 -containing gas, and is probably caused by increased O_2 chemisorption poisoning of the iron catalyst from irradiation excitation of the active sites.

Additional experiments are planned on this reaction, but with a catalyst prepared by the irradiation decomposition of iron pentacarbonyl in the adsorbed state.

CO_2 Decomposition

The heterogeneous irradiation decomposition of CO_2 in a flow system is being studied to determine the magnitude of energy transfer from the solid to

the adsorbed CO_2 and to evaluate any possible commercial uses. A flow system was constructed to operate at 100° to 600°C, 30 to 1000 psig, and 3 to 40 cc/min through a 30-cc reaction vessel. The gas-contacting materials are stainless steel, Monel, and miscellaneous inert material gaskets.

The semiconductor oxides used in these experiments include *p*-type NiO , *n*-type ZnO , and *i*-type $\eta\text{-Al}_2\text{O}_3$ and $\text{SiO}_2\text{-Al}_2\text{O}_3$, as well as Ag_2O and Ag_2O supported on SiO_2 . No CO yields were detected for the NiO and ZnO catalysts because of their small surface areas and because *p*-type and *n*-type semiconductor oxides were shown previously in capsule experiments to be least reactive to the decomposition of CO_2 . For the high surface area insulators, $\eta\text{-Al}_2\text{O}_3$ and $\text{SiO}_2\text{-Al}_2\text{O}_3$, there were no significant yields except at 500°C, where the *G*-values, based on irradiation energy absorbed in the gas phase only, ranged from 3 to 6. The radiation intensity from Co^{60} was 6.6 megarads/hr, and the CO was analyzed by gas chromatography on a molecular sieve column programmed from 60° to 250°C.

In a more detailed investigation of the decomposition on Ag_2O at temperatures from 100 to 450°C, pressures from 3 to 50 atm, and CO_2 flows from 5 to 40 cc/min, the *G*-value for CO formation was found to increase with flow rate at all temperatures and pressures and to decrease with increasing temperature and pressure. The maximum *G*-value of 8.5 occurred at 100°C, 3 atm, and 40 cc/min. These results are in agreement with the thermodynamics of the system; the equilibrium shifts in favor of CO_2 with increasing temperature and pressure. Additional work will be done at low pressure and temperature with different catalyst materials.

N_2 Fixation

The direct oxidation of N_2 from air or a synthetic mixture of O_2 and N_2 would provide an inexpensive method for the fixation of N_2 if a suitable "catalyst" could be found. Although the thermal equilibrium of

at room temperature is <1 ppb NO , radiation has been shown to completely convert air to NO_2 because the rate of the thermal back-reaction at room temperature is negligible.

A flow system of inert materials has been constructed in order to operate a 30-cc reaction

vessel at temperatures from 25° to 600°C, pressures from 15 to 3000 psig, and flows from 1 to 120 cc/min. The effluent is analyzed for NO and N₂O by temperature-programmed gas chromatography on a specially developed molecular sieve column, and for NO₂ and O₃ by spectrophotometric analysis. Radiation from Co⁶⁰ ranges in intensity from 0.7 to 6.5 megarads/hr.

A detailed investigation of the homogeneous irradiation fixation has been started prior to the development of a heterogeneous system in an attempt to understand the kinetics of the simpler case first. Initial results appear in Figure 4. There is no detectable yield of NO₂ without radiation, in agreement with the thermodynamics and kinetics of the thermal reaction. The time required to reach 3 ppm NO₂ without radiation at 600°C is 16,000 yr.

It can be seen that the *G*-value increases with flow rate and with temperature, especially at the higher flows, although the yield remains fairly independent of temperature and varies only with flow rate. A few experiments performed at two intensities indicate that the concentration is almost directly proportional to intensity. For ex-

Figure 4. Homogeneous irradiation of air (21% O₂, 79% N₂).

ample, at 100°C, 3 cc/min, 69 atm, and an intensity of 6.5 megarads/hr, the yield and *G*-value were 1460 ppm NO₂ and 0.98, respectively, compared with 172 ppm NO₂ and 0.99 at 0.76 megarads/hr. This precludes a chain reaction mechanism. Catalysts will be used to increase the utilization of incident radiation.

Other areas of research include the synthesis of ozone and the decomposition of adsorbed iron pentacarbonyl. O₃ is produced in the air irradiation experiments but only below 100°C because of thermal decomposition; this necessitates a separate investigation at low temperatures. Iron pentacarbonyl adsorbed on various high surface area materials will be decomposed by radiation and thermally for the preparation of metal-supported catalysts. R. DIETZ, T. SCHREINER

RADIATION EFFECTS ON ELECTRODE REACTIONS

The program to investigate radiation effects on electrochemical processes has been focused on improving the kinetics of the oxygen electrode reaction. This particular reaction is of interest in connection with fuel cell applications and with lowering the energy costs associated with water electrolysis. The irreversibility is traced to a kinetically slow electrode reaction rather than to mass transfer limitations. To date, all work has been done with the Co⁶⁰ γ source at HIRDL.

Table 6

Weight Losses of Selected Materials in Normal Acids
(*T* = 70°C, time = 24 hr, $\Delta W/S$ = mg/cm².)

Material	Acid		
	HNO ₃	H ₂ SO ₄	HClO ₄
Pt	negl.	+0.028 ^a	0.028
Pd	0.095	negl.	0.02
B ₄ C	0.107	0.046	0.015
Si	0.04	+0.08	
SS 347	0.155	negl.	+0.125
SS 304	0.20	0.25	0.13
Ta	0.015	0.045	0.033
Ti	0.022	diss.	0.020
W	0.15	0.03	+0.12
Au	negl.	0.10	negl.
Ag	diss.	0.19	diss.
Ni	diss.	1.2	1.2

^aPlus sign preceding indicates a weight gain.

Initially, materials were irradiated to evaluate their suitability for use in electrochemical studies. Borosilicate and silica glasses proved satisfactory, but most plastics were suspected of releasing contaminants upon irradiation. Compatibility tests were also conducted in both acids and bases to find metals with suitably low corrosion rates. Results for several acids are given in Table 6. Similar tests in basic solution at room temperature for 140 hr led to the finding that the following metals all corrode <0.2 mils/yr: Ag, Nichrome V, Zr, Mg, Monel, Kanthal, Au, Ti, and Pt. Ta and Ti passivate, and special irradiation tests were done for these metals. The metal corrosion rates were not found to differ from those for the unirradiated case, even when the highest dose rate (7×10^6 rads/hr) was used. A brief examination was also made of the influence of γ radiation on a variety of commercial electrolytic capacitors. Capacitance and dissipation factors were measured at 1000 Hz for Ta and Al electrolytics in the presence of 7×10^6 rads/hr γ radiation. In all cases there was no detectable change in parameters. In addition to the evaluation of materials as test electrodes, an investigation of the oxygen electrode was begun with use of Pt, at present the best-known catalyst, and radiation effects were studied. A polarograph was used to apply linear electrode potential scans from 0 to 2.5 V. The characteristics of the electrode are shown in Figure 5. The anodic and cathodic Tafel lines are drawn for increasing and decreasing potential. The entire cell was then exposed to 7×10^6 rads/hr. The dotted curve rep-

resents the shift in the potential current characteristic for the first complete scan during exposure. It can be seen that the anodic currents under irradiation are higher, the anodic slopes increasing and decreasing are the same, and the cathodic currents are lower. Subsequent scans showed progressive potential shift, which was traced to the buildup of radiolysis products in the perchloric acid electrolyte. These products obscure the study of the oxygen electrode. An analysis for Cl^- permitted the calculation of a G -value equal to 0.11 from ClO_4^{2-} . Work is currently under way with electrolytes that are more radiation stable. J. McNICHOLAS, W. HORN

RADIATION TREATMENT OF ACID MINE DRAINAGE

The possible use of ionizing radiation for the oxidation and removal of ferrous iron from acid mine drainage is being investigated. Drainage from the mines in the coal mining states of Pennsylvania, West Virginia, and Kentucky is contaminating the ground waters in the area so severely that state laws prohibit effluents containing >7 ppm Fe and acidities of $<pH$ 6. Current methods present the difficulty of removing iron in the ferrous state. Earlier radiation chemistry experiments with the Fricke Dosimeter had shown that when an organic impurity is present, a radiation-induced chain oxidation of ferrous iron could take place. This led to an investigation of the Co^{60} γ -radiation oxidation of raw acid mine drainage water obtained from the field.

Preliminary experimental data were obtained on the removal of ferrous iron from acid mine drainage by neutralization with limestone followed by Co^{60} γ -radiation treatment. At a pH of ≈ 5.7 after limestone neutralization and while agitating with air sparging, the dissolved ferrous iron content can be decreased from 409 ppm to <1 ppm in a period of time relatively short compared with that required when no radiation treatment is given. Thus radiation treatment appears to act as a catalyst in promoting the removal of ferrous iron from mine drainage. The rate of ferrous iron removal seems to be proportional to the square root of the intensity, indicative of a chain oxidation mechanism which would include a biradical chain termination step. The chain carrier may be hydroxyl radicals. An ex-

Figure 5. Potential current density characteristic of oxygen electrode.

perimental G -value of 148 was obtained at a radiation intensity of 20,000 rads/hr, and a rate of ferrous iron removal of 45 ppm/min was obtained at an intensity of 4.3 megarads/hr. Based on these experimental data, two irradiation processes are visualized. Co^{60} is indicated for a low-intensity, longer holdup time system, while an electron accelerator or a high-intensity isotopic source is indicated for a very rapid removal and low holdup process. An optimization between tank holdup and radiation source cost can be made. Cost and availability of source at the low-intensity condition seem to be reasonable for a million-gal/day plant removing 300 ppm ferrous iron. Further optimization and process development, in addition to experimental studies at lower temperatures to improve the yield, are required to further evaluate the radiation treatment process for comparison with the limestone-lime treatment process. An important favorable factor may be that the limestone-radiation process yields a readily separated crystalline precipitate, while the limestone-lime treatment usually produces a flocculent precipitate that is difficult to handle and dispose of. A number of Government agencies involved in water pollution control are interested in this process.

M. STEINBERG,
J. PRUZANSKY, L. JEFFERSON

SURVEY EXPERIMENTS

Desulfurization of Oil

Work has been initiated on desulfurization of oil and possibly coal by γ radiation. The approach to this work involves an attempt to oxidize the refractory organic sulfur compound thiophene into a water-soluble material which can be extracted from the oil. Pure thiophene, in the absence of air, was found to be radiation stable for a total dose of 3.7×10^7 rads. In the presence of water and air (2000 psi), the thiophene decomposed into a solid material. Sulfur analysis of the water fraction was negative. When thiophene and water alone were used, no decomposition to solids occurred. The water fraction, however, contained 0.84% sulfur, which may be attributed to the solubility of thiophene in water. With thiophene and air (2000 psi), the sample partially decomposed to a solid.

A sample of No. 6 fuel oil containing 2.63% sulfur, obtained from the BNL Plant Maintenance Division, was irradiated in the presence of water

and air (2000 psi). Analysis of the oil after irradiation showed a sulfur content of 1.22%. Further work is being carried out to determine G -values for removal of sulfur under various conditions.

Polymerization of Diglycol Carbonate

Diglycol carbonate monomer samples, tinted with various dyes, were polymerized by γ radiation at 20°C. This monomer polymerizes by a free-radical mechanism, and the polymer formed is used for making optics such as sun glasses and safety glasses. The purpose of this work was to determine the stability of the dyes at radiation doses high enough to polymerize the monomer. Conventionally the polymer is formed by initiating the reaction with benzoyl peroxide and heat. The use of benzoyl peroxide, however, results in the destruction of the dyes through oxidation. The optical quality of the polymer may also be affected by catalyst fragments. Visual observation of the irradiated samples indicated that the dyes had not been affected.

P. COLOMBO,
J. FONTANA

Fruit-Plastic Impregnation

An attempt was made to impregnate the outer skin of oranges with polymer in order to retard spoilage and increase shelf-life. Oranges were soaked for several hours in vinyl pyrillidone, styrene, and methyl methacrylate monomers. The average radiation dose required for complete polymerization was $\approx 4 \times 10^5$ rads. A weight loss of up to 20% was observed to occur in the oranges that had been soaked in monomer. After standing for two weeks at room temperature, no difference could be detected between the impregnated and control oranges. The oranges were cut open, and a "smell" test indicated that monomer had penetrated the skin. A panel of "testers" gave unanimous preference to the untreated oranges.

P. COLOMBO, J. FONTANA

Plastic Impregnation of Leather

Leather impregnation experiments have been conducted with vinyl acetate monomer. Pieces of cowhide were soaked in monomer overnight at 20°C. The samples were removed from the liquid monomer and irradiated by γ rays at 20°C until polymerization of the monomer was complete. The irradiated samples were as soft and flexible as the unirradiated samples. Water absorption

tests on the impregnated and control samples showed weight increases of 20 and 94%, respectively. Impregnation of leather with polymer can be effective in upgrading poor leather, improving water permeability and scuff resistance, and retarding mildew and rot.

P. COLOMBO,
J. FONTANA

HIGH PRESSURE LABORATORY

Two recessed γ cells have been constructed in the High Pressure Laboratory for use in the development of radiation-chemical processes. The cells, each containing $\approx 1.4 \times 10^4$ Ci Co^{60} , are designed for capsule and small flow experiments with liquid and gaseous materials. Protective equipment has been provided so that monomers

such as ethylene gas at 200°C and 2000 atm pressure can be used safely. Radiation source handling equipment includes a water storage pool with an integral source elevator in one cell (Figure 6) and a dry shielding cask with source-extracting mechanisms in the other. All other normal hot cell features are provided. Protective systems that are provided in each cell because of the explosive gas hazard include (1) combustible gas detection equipment, (2) a safe path for system pressure relief, (3) a gas inerting system, and (4) an explosion suppression system.

In order to provide a work area near the recessed γ cells, extensive modifications to the building were made. These included connecting two buildings with an addition ≈ 3000 sq ft in area, and constructing a blow-out type shed near the

Figure 6. Recessed γ radiation cell, showing source elevator and storage pool.

recessed γ cells to house gas compression equipment.

L. KUKACKA, D. HUSZAGH,
J. VARELA, K. KANIGE

Chemonuclear Program

M. STEINBERG

The scope of the chemonuclear program encompasses basic and applied research relating to the use of reactor radiation for the synthesis and production of industrial chemicals. This includes (1) radiation and fission fragment chemistry studies on economically promising endothermic reactions such as the fixation of nitrogen for fertilizer production, the synthesis of ozone for use in water purification, and the formation of CO by CO_2 decomposition for industrial gas production, (2) the development of fission fragment sources and fuels, (3) the construction and operation of an in-pile research loop for studying these systems in a flow system and investigating product contamination, and (4) the design and evaluation of entire chemonuclear process systems, including multipurpose complexes.

RADIATION AND FISSION FRAGMENT CHEMISTRY

N_2O Dosimetry

A calibration curve giving absorbed dose as a function of nitrogen concentration (Figure 7) has been experimentally determined. The following equation has been fitted to the curve.

Figure 7. N_2O dosimetry.

$$D = 21.5 (\% \text{N}_2) - 7.75,$$

where D = absorbed dose in 10^{20} eV/g and $\% \text{N}_2 = \text{N}_2$ concentration by volume.

Nitrogen Fixation

Homogeneous Gas-Phase Irradiation of $\text{N}_2\text{-O}_2$ Mixtures. The yield-dose curve for the fission fragment irradiation of a 77.3% N_2 -22.7% O_2 gas mixture at 57.5 to 69.5 atm pressure was completed. The yields of NO_2 and N_2O are shown in Figure 8; a continuous rise in NO_2 concentration with a $G(\text{NO}_2)$ value of 1.2 is indicated. The apparent differential increase in the $G(\text{NO})_2$ value observed in earlier experiments has been tentatively attributed to the displacement of the U-Pd fission foil to the walls of the vessel, which caused a decrease in energy absorbed.

Heterogeneous Irradiation of $\text{N}_2\text{-O}_2$ Mixtures.

The purpose of these experiments is to explore the possibility of developing methods of increasing the G -value for nitrogen fixation to a value greater by an order of 2 than that obtained in the homogeneous gas-phase experiments. A $G(\text{N})$ value of

Figure 8. Fission fragment and reactor irradiation [F.F., (n,p) , and γ] of a 77.3% N_2 + 22.7% O_2 gas mixture.

Table 7

N₂ Fixation

79% N₂-21% O₂ (Air) Gas Bubbling Through an Aqueous Column of Liquid in a Co⁶⁰ γ -Radiation Field
(Radiation intensity, 3.0×10^6 rads/hr; total dose, 15.0×10^6 rads; T , 50°C;
liquid volume in field, 100 cc; total liquid volume, 300 cc.)

Run No.	Liquid	Gas pressure, atm	Air flow, cc/min (STP)	Gas vol in field, cc	Concentrated fixed N		$G(N)$ total fixed (based on gas phase), molecules/100 eV
					N (oxide), ppm	N (NH ₃), ppm	
54	Distilled water	1	0	(0.95) ^a	0.018	0	(26.1) ^a
50	" "	"	6	0.24	0.06	0.14	1150
52	" "	"	60	1.50	0.37	0	34.1
55	" "	2	300	3.6	0.047	0	9.0
53	Distilled water	100	0	(95.4) ^a	0.29	0	(4.2) ^a
49	" "	"	600	0.24	0.35	0.28	36.1
56	" "	"	30,000	7.0	0.18	0	1.8
60	0.5 <i>N</i> NaOH	1.0	0	(0.95) ^a	0.11	0	(154) ^a
57	" "	1.33	30	0.72	0.22	0	430
58	" "	3.0	60	1.1	0.11	0	107
59	" "	1.0	300	2.4	0.11	0	21
63	0.5 <i>N</i> NaOH	100	0	(95.4) ^a	0.22	0.13	(3.2) ^a
61	" "	"	3,000	0.7	0.49	0	12.3
62	" "	"	6,000	1.5	0.42	0	3.9

^aFigures in parentheses in column 5 are the volumes of the N₂ and O₂ dissolved in the liquid in the radiation field, and those in the last column are the $G(N)$ values based on this volume. It is probable that the fixation of N in these experiments at no flow is due to occluded gas on the walls of the vessel which cannot be precisely accounted for.

6 or more is required for an economically competitive process.

Gaseous Nitrogen Pressurized Over Liquid N₂O₄. Co⁶⁰ γ -radiation experiments with nitrogen gas pressurized over liquid N₂O₄ have indicated some formation of NO and possibly N₂O₃ in the liquid phase. However, the yields were small, and the temperature-vapor pressure range of liquid N₂O₄ would place restrictions on the design of a reactor for production purposes. Other, more promising routes are being explored, as indicated below.

Gaseous N₂-O₂ Pressurized Over Solid Substrates. A series of Co⁶⁰ γ -irradiation experiments were carried out with N₂-O₂ gas pressurized over various solid substrates, including silica gel, alumina, molecular sieve, and manganese dioxide, in both the presence and absence of water. Silica gel gave the highest yield of nitrogen fixed; alumina gave the next highest. Increasing pressure enhances the yield. However, a large positive effect does not appear, and $G(N)$ values ≤ 2.8 were obtained in these experiments.

Gaseous N₂-O₂ Pressurized Over Water and Aqueous Solutions. An apparent large yield of fixed nitrogen both in the oxidized form as nitrate-nitrite (NO₃⁻ and NO₂⁻) and in the reduced form as ammonia (NH₄⁺) is produced when gaseous N₂-O₂ is pressurized over aqueous media. The total yield or $G(N)$ value based on energy absorbed in the total mass of liquid at the highest gas pressure of 680 atm is as high as 1.5, which indicates a $G(N)$ value running into the hundreds based only on the mass of nitrogen dissolved in the liquid. There does not appear to be any species in the aqueous phase that is energetic enough to break an N—N bond for fixing nitrogen. This leads to the conclusion that the nitrogen is being fixed in the gas phase in the form of oxidized and reduced N which is then absorbed in the aqueous phase. Experiments made in which gas-to-liquid mass ratios were varied confirm this conclusion.

Gaseous N₂-O₂ Bubbling Through Aqueous Media. The conclusions from the pressurized

gas experiments have led to a series of experiments in which N_2 - O_2 gas is bubbled through a column of liquid in a Co^{60} γ field. The NO_3^- , NO_2^- , and NH_4^+ formed in the gaseous bubbles are absorbed in the liquid, and the calculation of $G(N)$ is based on the gas phase. A summary of preliminary results is given in Table 7.

The yield appears to go through a maximum as the air flow is increased, which indicates a surface-to-volume effect probably caused by surface changes due to changing bubble sizes. The most encouraging facts are that a $G(N)$ -value >2 can indeed be obtained and that values higher than the thermodynamic value of 284 indicate energy transfer effects.

Fog Experiments - Liquid Fog in Gaseous N_2 - O_2 (Air). From an applied point of view, the most efficient manner of utilizing Co^{60} γ or reactor radiation is a high surface-to-volume and low liquid-to-gas mass ratio system where the gaseous phase is continuous. This pertains to a fog system of dispersed liquid droplets in gas, which allows maximum deposition of radiation energy in the gas phase. Initial experiments in a fog box with a central plaque of Co^{60} gave an encouraging $G(N)$ -value of >3 . Improvements in experimental conditions for further experiments are being made.

Fixation of Nitrogen in the Plume From the Brookhaven Reactor Coolant Stack. Samples of rain water taken around the Brookhaven Graphite Research Reactor (BGRR) stack indicated an increase in fixed nitrogen content (as NO_3^- and NO_2^-) directly underneath the plume. The increase in nitrogen content (by as much as a factor of 2) is attributed to the β radiation of decaying Ar^{41} acting on the N_2 - O_2 in the atmosphere. During a rain storm the liquid droplets absorb the NO_2 while falling through the plume. Some energy transfer effects may be occurring.

CHEMONUCLEAR IN-PILE RESEARCH LOOP

The construction, assembly, and installation of the Chemonuclear In-Pile Research Loop (CIRL) at the BGRR are nearly complete. The remaining work is primarily that of finishing the electrical power and instrumentation systems. Figure 9 shows the progress of the work on the out-of-pile section of the loop at the southwest corner of the BGRR.

During the year the last of the five main loop containments, T-3, was set in place on its supporting framework and was fitted with an access platform and ladder. This makes maintenance work on any of the mechanical components in the tank relatively convenient, once the tank cover is removed. This containment has been encased in 2-in.-thick lead shielding for the control of γ rays in case a rupture in the primary piping in one of the other containments releases radioactive gas to the common containment atmosphere.

The 40-ft-long in-pile section of the CIRL has been inserted in channels W-11 and E-11 of the BGRR. The operation, a delicate one, was carried out without incident. The section has been filled with nitrogen and is in standby condition, ready for use. The laminated Masonite and lead neutron and γ shielding panels have been fabricated and are being set in position. Placement of the remaining shielding panels will be done after final testing and calibration of the instrument systems and after the out-of-pile section has been operated, since access may be required to various parts of the complex.

The inlet and outlet pipes of the out-of-pile section have been connected by a temporary jumper. This makes it possible to operate the entire system under the full range of pressure, temperature, and flow conditions independently of the in-pile section. It considerably simplifies this phase of testing, since there is no possibility of circulating radioactive contamination or of interfering with reactor operation. An operating manual has been prepared outlining step by step the operating procedures to be followed. After reliable operation has been demonstrated, the final connections will be made to the in-pile section and the complete loop operated as a unit, but without fuel being loaded. Dosimetry measurements will be made by using N_2O , and the effect of reactor background radiation on the chemical systems of interest will be determined. Finally the loop will be run with honeycomb fuel elements in place.

Both gas-bearing compressors that were built to order for the CIRL have been received. The difficulties encountered with the Société Rateau centrifugal compressor at high speeds were resolved and the machine met performance specifications before shipment from Paris. The tests were witnessed by a representative of the Office of Naval Research, London. This compressor has been installed in the loop. A regenerative com-

pressor, built by Mechanical Technology, Inc., also met performance specifications. The variable frequency power supply bought for use with the loop was first shipped to MTI and used to drive their compressor during the test period. This afforded an opportunity to debug the power supply and ensure that it was properly matched to the compressor. It has since been shipped to BNL, set up, and checked out with the Rateau compressor as well. The MTI machine was to have been supplied with both rotor and stator canned for protection against the loop atmospheres. The rotor was satisfactorily canned; how-

ever, small leaks in the stator can, probably at the power feed-throughs, resulted in deformation of the can after exposure to gas at high pressure. Since the motor manufacturer could not supply a can that would take the pressure differential, the pump was accepted with an uncanned stator. In return, MTI supplied a second stator and an improved design for a stator can. This design was further modified and the can fabricated at BNL. The stator has been canned and tested, and the compressor is now ready for final assembly. This machine, which is corrosion and radiation resistant and lubricant free, has received a Vaaler award (top honors) for its unique design as a gas circulator. The two compressors are interchangeable in the loop, despite the differences in their mechanical and electrical designs.

Several problems arose in the development of the drive for moving the fuel carriage in and out

Figure 9. View from above of the T-3 and T-4 containments at the southwest corner of the BGRR. Lead slab shielding is being hung on T-3. At the right side of the open T-4 containment can be seen the Rateau gas-bearing compressor. The first level of laminated shielding panels is in place around T-4.

of the reactor core. Although the central pressure tube is free to move relative to the outer containment tube through a bellows connection, there was still sufficient distortion on heating and cooling to cause the 5-ft-long fuel carriage to bind up as it traveled along its guide tube. Several approaches to the problem were tried. The one adopted uses a flexible stainless steel tubing to hold the fuel units in position under spring pressure, and stainless steel straps to retain the end fittings. These fittings serve as anchor points for the drive cables and as handling tool attachments. The fuel package assembly is shown in Figure 10. The carriage is drawn into place at the center line of the reactor by using a Harmonic Drive unit to wind the attached cable onto a drum. The carriage is returned to its outboard position by action of a constant tension spring motor that winds up as the carriage is pulled into the core. The assembly as finally developed was operated under the full range of loop conditions in the cold loop test facility before the in-pile section was moved to the BGRR, and it behaved satisfactorily. The tracks for guiding the shields and accessories for charging and removing fuel elements were laid at the east face of the reactor, and the various fuel handling components were checked out.

At four positions on the out-of-pile section of the CIRL (i.e., at the inlet and outlet of the in-pile section and before and after the decontamination section), fission and γ ionization chambers are located to indicate the delayed neutron and γ levels in the process gas at these points. Since the fission chambers are considerably more sensitive to thermal neutrons than they are to the epithermal delayed neutrons, the chambers have been surrounded by Masonite moderator and boral and cadmium absorbers. In this way each fission chamber is shielded from neutrons from other parts of the system, particularly those that may have been moderated to thermal or near thermal energies. The neutron and γ chambers have now been calibrated so that they can be used to obtain absolute values of the flux levels, as well as relative data referring one part of the loop to another. Calibration was accomplished in one of the hot cells at the HIRDL with use of photo-neutrons produced by action of the 2.75-MeV Na^{24} γ rays on beryllium. These neutrons have an energy of ≈ 640 keV, close to the predominant delayed neutron energy of ≈ 600 keV. A 2-ft section of the pipe that will contain the process gas

and the two chambers in their mounting were mocked up in exact geometry in the hot cell, including the Masonite, boral, and cadmium neutron shielding. The pipe section was filled with a Be rod having a hole drilled along the axis to take a tube filled with sodium hydroxide. This tube was irradiated in the BGRR, transported to the HIRDL, and inserted in the hole of the Be. The neutron generation approximated that from a homogeneous emitter filling the pipe. The Na^{24} γ activity was measured by a standard ionization chamber in the cell. This value was then used to calibrate the γ counters and calculate the neutron flux seen by the neutron counters. After the calibration, the four pairs of chambers were inserted in their positions within the containments.

The analytical instruments have been installed in their individual containments and connected to the valve manifold by stainless tubing run through containment ducts. These instruments

Figure 10. Chemonuclear fuel package and carriage assembly, showing, on the right, the 2-in.-long honeycomb fuel units.

(mass spectrometer, gas chromatograph, photometer, and moisture analyzer) have all been modified for remote operation in gas-tight containments and have been calibrated. The duplex Corblin diaphragm compressor, used to repressurize the gas in the analytical loop for charging back into the main loop after sampling, required the reworking of its stainless steel heads by the manufacturer to correct a design fault that was causing the diaphragms to fail prematurely. After the pump was reassembled, the diaphragms gave satisfactory service under test, and the pump has been installed in the loop. The CIRL is expected to be ready for nonfueled operation early in 1968.

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CHEMONUCLEAR FUEL DEVELOPMENT

The pack-rolling process for producing ultra-thin foil has been refined to the point where the variation in the thickness of the foil can be controlled to within 10%. The process has been used to produce 0.0001-in.-thick foil for chemonuclear application. The alloy used is 20% fully enriched uranium and 80% palladium clad with a diffusion-

bonded layer of platinum equal to 10% of the base in thickness. Sufficient foil has been rolled to permit the fabrication of three 5-ft-long elements for use in the CIRL. These elements will be composed of units 1½ in. in diam and 2 in. long, in three different cell sizes – 0.040, 0.125, and 0.250 in. across the flats, respectively. Enough units are on hand to make up a 22-in.-long element of the smallest cell size and 60-in. elements of each of the other two. The honeycomb is made by the Hexcel Corp. with use of a diffusion bonding process that introduces no flux or foreign bonding material. The formed honeycomb is trimmed to the desired cylindrical shape and mounted in a 2-in. length of stainless steel tubing by means of spot-welded stainless anchor strips. Figure 10 shows a number of these units before being loaded into a fuel package and carrier assembly.

Some characteristics of the fuel element material are shown in Table 8. Included is the calculated efficiency of fission fragment energy deposition for pressure and temperature conditions that are of interest in the operation of the CIRL.

Work is continuing on a method of producing chemonuclear fuel elements by coextrusion developed at the Pacific Northwest Laboratory of Battelle Memorial Institute. In this method rods of a Cu-Ni alloy are coated with enriched U-Pd in the proper proportion and clad with a vapor-deposited layer of Pt. A number of rods are bundled together and placed in a jacket, and the entire assembly is then extruded through a cylindrical die. Dimensions of the various components are selected so that the final extrusion results in a honeycomb of clad U-Pd with a 0.030-in. cell set in a matrix of Cu-Ni alloy. This "sacrificial" matrix is then dissolved, leaving the desired fuel configuration. A 5-ft-long element has been prepared. Experiments are now being run on slices of the element to establish the most satisfactory agent and conditions for dissolving the matrix in a reasonable length of time, while leaving the fuel network intact.

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Table 8			
Properties of Honeycomb Chemonuclear Fuel Elements			
		Honeycomb dimension across flats	
		0.040 in.	0.125 in.
Enriched uranium (93.3% U ²³⁵), weight per foot of fuel element		4.45 g	1.41 g
Power per foot of fuel element at thermal flux of 10 ¹² n/cm ² -sec		325 W	101 W
Fission Fragment Energy Deposition Efficiency in Air			
Pressure, psig	Temperature, °F	0.040 in.	0.125 in.
75	–20	0.05	0.19
105	–20	0.06	0.21
500	–20	0.21	0.27
75	100	0.05	0.17
105	100	0.06	0.20
500	100	0.21	0.27
1000	1000	0.21	0.27

ECONOMICS AND EVALUATION OF CHEMONUCLEAR AND NUCLEAR COMPLEX SYSTEMS

ORNL Agro-Industrial Complex

Assistance was given to ORNL for their concept of large water-industrial-agricultural nuclear-

based complexes. The descaling process used in desalting water results in the generation of large amounts of CO_2 by-product. A synthesis was proposed, as requested by ORNL, which converts CO_2 to polyvinyl chloride resin; this also utilizes by-product Cl_2 produced from electrolytic cells. BNL personnel also assisted in establishing ground rules and participated in concept discussions.

Salton Sea, California, Nuclear Desalting and Power Complex

A study was made of the feasibility of using nuclear desalting plants in the Imperial Valley Region of California. The area has arable land that could produce high-value crops, but no water is available except that from the Colorado River, which is already fully used. Another problem is the increasing salinity of the Salton Sea, an inland saline sea in the area that acts as a runoff basin for brackish irrigation water. The salinity rate increase indicates that fish in the Salton Sea, which is a developed recreational resource, will cease reproduction in about 20 years, when the salinity is expected to reach 40,000 ppm.

The study indicates that either of two schemes will serve to increase the available water by 800 million gal/day, stop the salinity increase, and add 2000 MW(e) to the power grid. The power could also be used to produce fertilizer for the area and for export.

Table 9 gives the parameters for the two systems. One cycle uses a split desalting plant at the Salton Sea and at an ocean site. Fresh water is pumped from the ocean site to the valley, and

part of the brine concentrate from the Salton Sea plant is pumped to the ocean to maintain salinity levels. The second cycle uses a single plant at the Salton Sea. Brine is pumped from the ocean to the plant, and part of the concentrated desalting plant effluent is pumped back to the ocean to maintain the Salton Sea salt concentration. The desalted water will make it possible to bring an additional 200 sq miles under cultivation. M. BELLER

Nuclear Transformation of Fission Product Waste

An alternative to perpetual storage of long-lived radioactive fission product wastes (10.3-yr Kr^{85} , 28-yr Cs^{137} , and 30-yr Sr^{90}) has been conceived and evaluated. It consists of neutron absorption and transformation of these nuclides to shorter half-life or stable nuclides. A preliminary measurement of the thermal neutron cross section of Kr^{85} in the HFBR indicates values between 20 and 60 b. Thus Kr^{85} can be transformed after isotope separation in a fission reactor at fluxes between 10^{15} and 10^{16} . A reduction in half-life from 10.3 yr to several months can be obtained. Because of their lower absorption cross sections, Cs^{137} and Sr^{90} must be transformed in an intense neutron generator where neutrons are efficiently generated by a BeV-energy proton beam from an accelerator bombarding a heavy liquid-metal target. The use of the complex consisting of a nuclear power reactor, high energy proton accelerator, and spallation reactor offers an alternative to storage in perpetuity at a relatively minor additional charge of the order of 1 to 2% of the cost of power generation.

Table 9
Desalting Plant Parameters

	Split plant			Single plant and pipeline
	Salton Sea	Ocean site	Total	
Reactor power				
MW(t)	4,000	6,000	10,000	10,000
MW(e)	800	1,200	2,000	2,000
Water production (0.9 load factor)				
Gal/day	320×10^6	480×10^6	800×10^6	800×10^6
Acre-ft/yr	3.24×10^5	4.86×10^5	8.1×10^5	8.1×10^5
Added irrigation water runoff				
Acre-ft/yr			3.24×10^5	3.24×10^5
Salton Sea evaporation due to nuclear heat				
Acre-ft/yr			0.2×10^5	0.4×10^5

Radiation Engineering

J.H. CUSACK

HIGH INTENSITY RADIATION DEVELOPMENT LABORATORY

Operations

Source Inventory. The Co⁶⁰ inventory increased substantially this year (see Table 10) in support of the evaluation of Mark II and very high specific activity sources and of general experimental requirements.

A reinspection of all sources at the HIRDL was made; it was decided to dispose of all Al-clad flat sources and tubular sources and certain older, stainless steel clad sources because of the low activity, high percentage of leakers, and high cost of reclamation.

Source Services. A 400,000-Ci Co plaque was set up for other members of the Division and used for N₂ fixation experiments and concrete-polymer irradiations. Six Natick sources were leak-tested, cleaned, and shipped to the University of Notre Dame. A BNL tubular source, which had been sold to the Mellon Institute, was leak-tested, cleaned, and returned to the Institute. A Co therapy unit was reloaded for Bellevue Hospital with a 1000-Ci Oak Ridge teletherapy source.

Blood Irradiator. The Medical Department's Mark II blood irradiator was repaired after a minor operating mishap, and a new interlock was installed to prevent a repetition of the trouble.

Gamma Facility. A summary of the use of the facility by BNL groups and off-site researchers is given in Table 11.

HIRDL Conveyor System

Modifications were made to the HIRDL conveyor system to permit selection of the mode of

operation. Either a moving source with intermittently moving packages or a stationary source with continuously moving packages may now be chosen. The in-cell electrical equipment was simplified to improve reliability. Other modifications were made to increase the capacity of the system from 20 to 40 packages/hr. To handle this increased capacity, the loading and unloading areas have been expanded and truck docks added.

New Underwater Gamma Facility

The underwater γ irradiation facility at the HIRDL has become inadequate in terms of number of tubes, dose rates, work space near the facility, and safety. A new facility has been designed and is now under construction in the HIRDL annex. It will be housed in a 10 $\times$ 12 $\times$ 12-ft-deep stainless-steel lined pool equipped with a water treatment system. The annex is adequately isolated from traffic in the HIRDL area and has substantial space surrounding the pool for auxiliary experimental support equipment.

The pool will contain twenty-one 4-in.-diam underwater Co⁶⁰ dry-tube irradiators ranging in dose rate from 10³ to 10⁸ rads/hr. One special variable dose tube will be available for short-term emergency use. Each tube will be individually lead-shielded in the vicinity of the source cage to prevent "cross talk" between the tubes and to eliminate the 200-keV backscattered γ rays from the water. Each tube will be equipped with a semi-automatically operated quick-remove lead cap and a shielded sample carrier to minimize exposure of personnel during the introduction and removal of samples.

RADIATION PHYSICS

Dosimetry

During the year long-range stability studies were carried out on the standard Fricke dosimeter,

Table 10

Sources Received, 1967

Isotope	Type	Ci	No. of sources	Approx specific activity, Ci/g	Received from
Co ⁶⁰	Mark 1	790,000	176	70	Secondary encapsulator
Co ⁶⁰	Mark 2	594,000	94	125	Savannah River Plant
Co ⁶⁰	Mark 1*	464,000	40	560	" " "

*29 slabs 3 in. long, 11 slabs 6 in. long.

the deaerated Fricke dosimeter, the ceric sulfate dosimeter, and the Perspex HX dosimeter. Development and evaluation of the Perspex HX dosimeter were completed. Preliminary studies and evaluations were made of the cellulose acetate butylate dosimeter and an "effects" dosimeter for red western wheat. Exploratory studies were made of some new applications of oxalic acid and cyclohexane as dosimeters.

A portable and inexpensive thermoluminescent dosimeter readout covering the food process dose range was developed.

The third biannual dosimetry workshop, sponsored by the Division of Isotopes Development, US AEC, is in the final planning stage. It will be an international meeting and will be held in March 1968 at the U.S. National Bureau of Standards, Washington, D.C. The organization and planning of this meeting is a joint effort between BNL and NBS personnel.

BNL has this year cooperated with the ASTM in setting up and participating in large-scale test evaluations of two dosimetry systems: the oxalic acid dosimeter and the ferrous cupric sulfate dosimeter. Standard test procedures for the Perspex HX dosimeter and the deaerated Fricke dosimeter have been written and are awaiting release.

Perspex HX Dosimeter. Perspex HX, the British counterpart of UVT Lucite, was developed specifically for dosimetry (γ ray as well as charged particle) purposes. It is manufactured by Imperial Chemicals Industries, Ltd., London, under the

guidance of and in cooperation with the United Kingdom Panel on Gamma and Electron Radiation.

The Perspex samples used in this evaluation were 5 mm wide, 10 mm high, and 1.0 mm thick. The material was tested for its γ -ray dosimeter properties by using Co^{60} as a source.

The results of the evaluation studies indicate that upon irradiation Perspex HX develops an optical absorption spectrum composed of two superimposed peaks: a major peak, at $\approx 265 \text{ m}\mu$, and a less intense peak at $\approx 290 \text{ m}\mu$. The induced optical density at all wavelengths between 260 and 300 $\text{m}\mu$ bears a linear relationship to total dose over the range 10^5 to 3×10^6 rads. These measurements were reproducible with a standard error of $\pm 2\%$ and an error of $\pm 4.5\%$ at the 90% confidence level.

When tested against the standard and modified Fricke dosimeters, the Perspex displayed no significant dose-rate dependence between 10^5 and 7×10^6 rads/hr, provided that the temperature during irradiation was not allowed to rise above 60°C .

Isothermal and isochronal bleaching studies indicated that bleaching constants were relatively low. At temperatures below 40°C , the bleaching rate was $\approx 1.0\%/hr$ for total doses up to 5×10^6 . Between 40° and 60°C the bleaching was as high as 2 to 3%/hr, while above 60°C the bleaching rate rose sharply to $> 10\%/hr$ at 70°C . These bleaching rates are not considered high when compared with those of the UVT Lucite dosimeter, which bleaches at rates of 1 to 6%/min at 40°C .

The material was found to require a stabilizing dose of 0.25 megarads prior to use or calibration. The calibration constant or radiation sensitivity after predosing was found to be stable to within 5.0% over a three-month period.

Effects Dosimeter. Exploratory experimental investigations were conducted to determine the feasibility of using wheat itself as an "effects" dosimeter in grain irradiators. Preliminary results carried out on water extracts of wheat indicate that radiation-induced color changes in the wheat extracts, measured on a Dk-1 spectrophotometer in the region of 235 to 300 $\text{m}\mu$, bear a linear relationship to absorbed dose from 10 to 50 kilorads, the dose range of interest in disinfestation of wheat. The radiation-induced subtraction spectrum of water extracts of wheat for several total doses is shown in Figure 11.

Table 11
Use of HIRDL Gamma Facility,
November 1966 Through November 1967

	Use, hr
Nuclear Engineering	36,321
Alternating Gradient Synchrotron	4,851
Chemistry	1,274
Physics	886
Biology	260
Graphite Research Reactor	68
Cosmotron	62
Instrumentation and Health Physics	48
Off-site researchers	20
Medical	1
Total	43,791

There were 4560 samples irradiated in 2117 separate irradiations.

The radiation-induced changes observed in these studies are similar to those previously observed for sugar in a radiation field and are probably due to the presence of sugar in the grain. This assumption will be tested by chemical analysis. The use of an "effects" dosimeter of this type may serve to eliminate uncertainties arising in the measurement of dose due to geometry, radiation energy effects, linear energy transfer effects, and the effects of bulk flow in grains.

Thermoluminescent Dosimeter Readout. A thermoluminescent dosimeter (TLD) readout designed at BNL to operate in the food processing dose range was built, tested, and calibrated during the year. This readout system is different from any that are commercially available in that it is inexpensive ($< \$1000$) and portable (30 lb). Since it uses a solar cell as its light-sensing device, no sensitive micromicroammeter, photomultiplier tube, or high voltage supply is required.

The system can read out doses from 10^3 to 5×10^5 rads by using the standard LiF dosimetry powder, and it can be used in the megarad range by using special high-purity LiF or CaCO_3 . The instrument is capable of accurate and reproducible determination of dose with a standard error of $\pm 2.5\%$ and an error of $\pm 6.5\%$ at the 90% confidence level, based upon 150 separate calibration measurements.

The first instrument of this design (Mark I) was installed aboard the Portable Cesium Irradiator truck as its main dosimetry system. A second improved unit (Mark II) is now in use at BNL.

Figure 11. Absorption spectra of water extracts of Co^{60} -irradiated wheat.

Cellulose Acetate Butyrate Film Dosimeter. Thin strips of cellulose acetate butyrate film, 0.5 mm thick, were evaluated as a high megarad dosimetry material. The material was found to develop a radiation-induced optical absorption spectrum in the region from 280 to 360 $\text{m}\mu$, with an absorption peak at 295 $\text{m}\mu$. Measurements made of ΔOD vs total dose at 320 $\text{m}\mu$ indicated a linear dose-density relationship between 1 and 55 megarads (see Figure 12).

Isochronal and isothermal bleaching studies revealed that the induced optical density undergoes essentially no bleaching at room temperatures over long periods of time. At 40° and 50°C , however, the thermal bleaching rate rises sharply to $\approx 10\%/\text{hr}$.

Since the interest in this material at BNL is as a low-temperature, high-dose, in-cell dosimeter for monitoring the accumulated dose to HIRDL components, further evaluations are in progress.

Effect of Plastics on Fricke Dosimetry Solution. Studies of the effect of plastic materials (polyethylene, Tygon, and Teflon) on the normal operation of the Fricke dosimeter (ferrous ammonium sulfate solution) were carried out to determine the possibility of using these plastics in intimate contact with the dosimetry solution as containers and gasketing materials in flow systems.

Each of the plastics was found satisfactory for use with the dosimetry solution provided that a

Figure 12. Linearity of cellulose acetate butyrate dosimeter at 320 $\text{m}\mu$.

proper preconditioning procedure was used. The procedure evolved consists of sequentially rinsing the plastic in ferrous sulfate solution, irradiating it in the presence of ferrous sulfate solution to a total dose of 50 kilorads, rinsing in distilled water, and rinsing in fresh ferrous sulfate solution.

When preconditioned in this manner the plastics had no adverse effect upon Fricke dosimetry solution up to accumulated absorbed doses of 10^6 rads. The plastics did not cause spontaneous oxidation of the unirradiated solution and did not result in spurious increases in the G -value for the oxidation of ferrous ion in the radiation field.

Cs¹³⁷-Co⁶⁰ Heterogeneous Target Comparisons

Co⁶⁰ and Cs¹³⁷ source plaque dose distributions were compared in heterogeneous target configurations. For both isotopes, the heterogeneous target results were also compared with results from homogeneous targets bearing identical effective bulk densities.

Typical dose uniformity ratios ($\text{dose}_{\text{max}}/\text{dose}_{\text{min}}$) are presented in Table 12 for the two-sided irradiation of heterogeneous targets consisting of "close-packed," staggered arrays of 300×407 (3 in. in diam by $4\frac{1}{16}$ in. high) food cans with an effective density of 0.85 g/cc, and of homogeneous targets having the same effective density.

These data indicate that for target thicknesses up to ≈ 11.0 in. the dose uniformities in Cs- and Co-irradiated homogeneous targets are essentially the same.

Improvements in dose uniformity of 4 to 8%, attributable to γ -ray streaming in the target, were found in heterogeneous arrays irradiated with Co⁶⁰. Improvements in uniformity of 3 to 5% were also observed in Cs-irradiated heterogeneous

targets up to 5.5 in. thick. Dose distributions, however, were found to be less uniform in Cs-irradiated heterogeneous targets >5.5 in. thick when compared with homogeneous systems of the same density.

The decrease in uniformity in thick Cs-irradiated heterogeneous targets is thought to be due to absorption of low energy γ rays by the metal cans. This assumption is now being tested.

Comparisons of this type are being extended to heterogeneous target systems with effective bulk densities of 0.1 to 1.0 g/cc. Food cans of various diameters (up to 6 in.) are being used.

COMPUTER CODES

FUDGE Series

The FUDGE program was modified to eliminate oscillation of results by internally integrating within zones defined by the discontinuities at the corners of the rectangular source. Additional minor modifications were included to eliminate machine errors.

Further modifications were made to the code (FUDGE 5 series) to calculate the sum-total dose rate for intermittent "dwell" type irradiators (as contrasted with continuously moving target systems). A program was written for a system of two parallel passes on each side of the source; each pass consisted of 15 targets (5 horizontal by 3 vertical).

A subsequent modification based on the FUDGE program was written to calculate dose rate distribution and sum-total dose rates in intermittent dwell type irradiators of any size.

QAD Series

The QAD shielding program, originated at Los Alamos for reactor shielding, was adapted for use on the CDC 6600 computer for the solution of γ irradiator problems. Basically the program uses a point source integration method and therefore is capable of treating cases involving a wide range of source and target geometries and materials. It can readily handle source or target overlap.

The QAD J01 code was written for a static rectangular source and target.

The QAD J02 code solves cases involving a finite moving rectangular target with or without target reversal on each side of the source.

The RAD-K13 program is based on the QAD program and is for arbitrary size, shape, isotope, and

Table 12

Uniformity Ratios for Co⁶⁰ and Cs¹³⁷ Irradiation
(12×12 in. plaques; two-sided irradiation;
effective density of targets, 0.85 g/cc.)

Over-all target thickness, in.	Co ⁶⁰		Cs ¹³⁷	
	Hetero- geneous	Homo- geneous	Hetero- geneous	Homo- geneous
3.0	1.06	1.14	1.08	1.14
5.52	1.31	1.42	1.35	1.40
8.1	1.77	1.86	1.86	1.82
10.7	2.31	2.50	2.68	2.45

activity of source. It permits the inclusion of self-absorption, source overlap, target overlap, source cladding material, flux flattening absorbers, air gap, direct target exposure, or target reversal. It prints out the location of points of maximum and minimum dose rate and the corresponding dose rates, the ratio of maximum to minimum dose rate, and the source utilization efficiency.

RAD-K13G, a version of RAD-K13, is a more general program in which the source specific activity may be varied over the source volume for up to 10^5 source subdivisions; each isotopic source may have a source spectrum containing 30 discrete γ photons, and each absorber may be composed of 1 to 6 elements. A generalized geometry input may include as many as 50 homogeneous zones, bounded by not more than 50 surfaces. Zones may consist of up to 20 materials of 40 components each.

The RAD-K13F version solves the intermittent dwell irradiator case based on point source integration as contrasted with the Gauss quadrature integration used in the FUDGE series.

SOURCE EVALUATION

Simulation of Cs¹³⁴ and Cs¹³⁷ Production

γ Power calculations were performed for the Cs products separated from spent fuel elements at various levels of fuel burnup and post-shutdown waiting time. In all cases, Cs¹³⁷ was constant at about 32 wt % of total Cs; Cs¹³⁴ varied up to 2.6 wt %. A small amount of Cs¹³⁴ has a very large effect on the γ power of the source because of the high γ energy (1.565 MeV/disintegra-

tion) and short half-life (2.25 yr) of Cs¹³⁴ compared with Cs¹³⁷ (0.567 MeV/disintegration, 30 yr). Table 13 summarizes the relative γ power of Cs sources after various waiting periods.

PORTABLE IRRADIATORS

Portable Cesium Irradiator

The Portable Cesium Irradiator (PCI) is a 40,500-lb trailer-mounted unit with a capacity of 70 megarad-lb of unit density material per hour. It was designed by the Parsons-Jurdens Corp. to perform intermediate-scale in-the-field irradiations. The irradiator (Figure 13) was fabricated by the American Nuclear Corp. for the US AEC and shipped to the HIRDL for installation of 190,000 Ci of doubly encapsulated Cs¹³⁷ and for testing and calibration.

In use, two packages are placed in a loading chamber, the outer door is closed and an intermediate door opened. A shuttle then transfers the packages into the irradiation chamber, one above and one below the source plaque. After the desired dwell time has elapsed, the process is reversed.

A number of modifications and additions were made to the unit in the interest of safety and reliability, including the mounting of a radiation-sensing device in the loading chamber as an added safeguard against personnel exposure and the addition of a 6-in. I-beam structure to prevent accidental opening of the unit in case of upset.

BNL was also responsible for outfitting the trailer with lighting fixtures, furniture, and radia-

Table 13
Cesium-134 Specific Gamma Power

Initial weight % Cs ¹³⁴	Time out of reactor, yr									
	0.25		1.25		2.25		5.25		10.25	
	(a)	(b)	(a)	(b)	(a)	(b)	(a)	(b)	(a)	(b)
1.0	0.1101	54.1	0.0809	47.0	0.0594	39.9	0.0236	22.1	0.00506	6.38
2.0	0.2201	70.2	0.1618	63.9	0.1188	57.1	0.0471	36.1	0.01012	12.0
2.6	0.2861	75.3	0.2101	69.9	0.1542	63.3	0.0613	42.4	0.01316	15.0
Cs ¹³⁷ *	0.0936**		0.0914		0.0894		0.0834		0.0743	

(a) Cs¹³⁴ γ power in watts/gram of total Cs.

(b) % Cs¹³⁴ γ power.

*Cs¹³⁷ γ power in watts/gram of total Cs.

**Cs¹³⁷ concentration = 32.0% by weight.

tion dosimetry equipment. A BNL Mark I TLD readout and LiF-TLD dosimeters were supplied as the unit's main dosimetry system.

Prior to release of the PCI to Isotopes, Inc. (operating contractor), dose distribution characterizations were performed by using heterogeneous and homogeneous targets. The homogeneous target densities used were 0.12, 0.62, 0.88, and 0.964 g/cc, with target thicknesses ranging from 5 to 7 in. Most of these calibrations were performed on the 6-in.-thick target. The heterogeneous targets consisted of commercial packages of potatoes and mushrooms, two of the products to be handled by the irradiator in the field.

The object of these standardizations was to determine the dose due to dwell time at the maximum and minimum dose points in the target and the dose due to transit time at these same positions. The characterizations were carried out for both one- and two-sided irradiations. Typical results are presented in Figure 14 for a two-sided irradiation of a 6-in.-thick homogeneous target with a density of 0.964 g/cc.

Shipboard Irradiator

Dose distribution characterization of Shipboard Irradiator No. 2, formerly located in Gloucester, Mass., is being conducted at BNL in conjunction with the inspection and replenishment of the irradiator prior to shipment to its new location in Iceland.

Calibrations were performed prior to disassembly of the unit by using a homogeneous target (density, 0.6 g/cc) and standard Fricke dosimeters. The dose rates at the maximum and minimum dose points were found to be 17,500 and 12,000 rads/min, respectively. This corresponds to a uniformity ratio of 1.5 for dwell times which are long compared with the transit time of the irradiator. The transit dose at the maximum and minimum dose points was 4200 and 2750 rads, respectively.

Brookhaven Portable Cesium Development Irradiator

This irradiator, designed at BNL, utilizes a moving source plaque placed between two large irradiation chambers. The plaque is stored in a shipping cask which is attached to the irradiation chamber when in use. While in transit the plaque in its cask is handled separately from the other irradiator components. The total weight of the unit (Figure 15) is ≈ 18 tons, and its volume is 300 cu ft.

Figure 13. The Portable Cesium Food Irradiator, being prepared for visits to New England and other areas in a demonstration program. The entire irradiator, which has a 190,000-Ci source of Cs^{137} , weighs 40,500 lb. The aluminum and steel trailer is 35 ft long and 8 ft wide. Many test runs on grain, mushrooms, and other foods have been made at BNL with this irradiator.

Figure 14. Characterization of the Portable Cesium Irradiator, using a 6-in.-thick target (density, 0.964 g/cc). Transit dose at max dose point, 950 rads; at min dose point, 350 rads. Dose rate in dwell position at max dose point, 359 rads/sec; at min dose point, 216 rads/sec.

Figure 15. Model of Brookhaven Portable Cesium Irradiator.

The two irradiation chambers are $\approx 8 \times 27 \times 54$ in., and the source plaque measures 18×27 in. Tubing and piping for the irradiation of fluids can be inserted through stepped plugs. In normal operation, the lead shielding doors are interlocked with the source plaque. With the doors removed, the unit can be adapted to two-pass irradiation by adding external shielding and a conveyor system.

Two of these units are being fabricated by an outside contractor; they will be placed on loan by the US AEC to India and Argentina.

TECHNICAL ASSISTANCE

Irradco

This year Irradco was awarded a US AEC contract for the design and construction of a meat irradiation plant and for the large-scale irradiation of meat products. At the request of the AEC, BNL is providing technical assistance in the following

areas: preliminary design studies; modification of existing computer codes and development of new codes to more efficiently solve the "shuffle-dwell" irradiator concept involved in Irradco's design; selection or development of appropriate dosimetry systems; and design and setup of experimental studies to verify calculated dose distribution with use of the HIRDL facility.

Standard Calibration of Facilities Supported by the US AEC Division of Isotopes Development

A program was begun for the evaluation of dosimetry and irradiator calibration practices at all AEC-DID facilities involved in research in support of FDA petitions. The cross calibration of the dose measurements at the facilities with those at BNL, the calibration of the facility with use of standard dosimetry procedures, and personnel training will be undertaken where necessary.

The program has been initiated at the following facilities: the Marine Products Development

Irradiator Facility at Gloucester, Mass.; the Research Irradiator at MIT, Cambridge, Mass.; the USDA Stored Products Research Laboratory, Savannah, Ga.; College of Fisheries, University of Washington, Seattle; Bureau of Fisheries, Seattle; Oregon State University, Corvallis; Department of Pomology, University of California, Davis; and the Hawaiian Development Irradiator, Honolulu.

Extensive irradiator calibrations were performed at the MPDI facility in Gloucester and the MGI facility at Davis. At all the other facilities, Fricke dosimeter standardizations using standard ferric ion solutions were made. The results of these standardizations revealed no serious discrepancies or faults in dosimetry practices at any of the AEC-sponsored facilities.

Plans are under way for evaluations of the facilities at Louisiana State University, Baton Rouge; University of Michigan, Ann Arbor; and Michigan State University, East Lansing. Further evaluation and extensive calibration of the HDI in Hawaii are planned.

SOURCE DEVELOPMENT

Co⁶⁰ Radiation Sources

Final agreement between the AEC's Savannah River Plant and BNL was reached on specifications and quality control tests for the Mark II and III bonded sources. A pilot development order for 60 Mark III pieces was received from Nuclear Metals, Inc.; these will be activated next year.

Metallographic examination of a prototype Mark IV niobium-clad specimen showed that cladding thicknesses ranged from 7 to 15 mils. Bond quality was good and the electrode weld had good penetration, but some porosity and cracking were found. A thermal cycling test in air between 95° and 500°C showed that an oxide film formed within one day and that most of the Nb was removed at the end of 192 hr. Care must be taken, therefore, to keep individual first-encapsulated slabs separated until the protective second encapsulation is completed.

Sr⁹⁰ Radiation Source, Mark I

Inactive prototype specimens were received from ORNL. Metallographic examination showed that the first (cold) end weld was of good quality. A void about 1 mil thick was found between the

stainless steel cladding and the aluminum matrix. No evidence was found of a thermite-type reaction between the Al and SrSiO₃ microspheres. A variation in concentration of SrSiO₃ particles from top to bottom of the specimen was found, together with a wide range in individual particle density.

ORNL has recently developed techniques to avoid the hot end weld Al contamination problem and to maximize the matrix density. Preparations were made for production at ORNL of active Sr⁹⁰ microspheres.

Source Testing

Ten Mark II slabs that had been rejected after dye penetration test were examined under the microscope. Nine were found to have observable defects. The dye penetrant test was rerun on the remaining slab, and it passed the test. In the future, rejects from dye penetrant tests will be examined microscopically for confirmation.

Corrosion Studies

Hawaii Development Irradiator Sources. About 217,000 Ci of Co⁶⁰ radiation sources of the BNL Mark I type were shipped from BNL to Honolulu for use in the HDI. The casks were exposed on the top deck of the ship during the 4-week transit period. When the shipping casks were opened in the HDI pool, black precipitate matter arose from the casks. Radioactivity was reported at the pool ion exchanger; the surface of the pool had an activity of about 12 mR/hr.

The major factor causing the extra-source activity was corrosion of the source cladding that penetrated to the Co core. Sea water had apparently penetrated the casks through poorly fitted gaskets, and corrosion was probably due to the combined effect of low pH, the presence of dissolved metallic salts (halides), high temperature, and lack of oxygen.

After their return to BNL, severe corrosion was observed on each of the 24 source elements examined (Figure 16). It extended about 3 to 4 in. along the major axis and corresponded to the depth of liquid found in the shipping cask on its arrival at BNL. A bubble test showed that 22 of the 24 specimens had been penetrated. The outer claddings of the two nonleakers and the two worst leakers were removed. The inner claddings of the two nonleakers were not penetrated; those of the two worst ones were. It is probable that most of the remaining primary encapsulations leak.

Figure 16. Severely corroded BNL standard Co⁶⁰ source strips being removed from shipping cask after return from Hawaii.

A long-range experimental study has been initiated in an attempt to reproduce the corrosive environment noted in this shipment. The limits of safe exposure in terms of such factors as temperature, salt concentration, and oxygen will be determined.

Meanwhile, new sources have been successfully shipped to the HDI. Conditions of shipment (i.e., adequate gaskets and cocoons) were such that a bone-dry cask cavity was ensured. Even though the ship passed through a hurricane and suffered extensive deck damage, the sources (which traveled as deck cargo) arrived in as-shipped condition.

Cycling Tests. Forty-five cycles of the HIRDL pool-air cycling tests were completed. Results of weight change measurements on 16 irradiated and 16 unirradiated (control) stainless steel specimens were: control, +0.1 mg; irradiated, +0.9 mg. The difference between control and irradiated specimens was not statistically significant. A weight change of 0.9 mg would correspond to a corrosion rate of about 10^{-4} mils/yr, assuming the weight gain to be due to oxide formation.

Work was started on an automated cycling apparatus.

HIRDL Source Plaque. Weight change measurements were made on corrosion test specimens from a HIRDL plaque that had been exposed to the HIRDL environment for 84 weeks. The 12 specimens were dummy second-encapsulation tubes inserted as spacers in the plaque. The average weight gain was 1.8 mg per specimen, disregarding two anomalously high weight gains which were probably due to end leaks. If this average gain is assumed to be due to oxide formation, the corrosion rate is about 2×10^{-4} mils/yr. This gain may indicate that a corrosion induction period has ended and that corrosion is beginning.

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Exploratory Research and Development

RADIATION CHEMICAL REACTOR STUDIES F. HILL

In these studies the principles of design and operation of radiation chemical reactors are investigated. During the past year studies on isothermal reactors have been continued and broadened considerably. Work on the radiation treatment of liquids and particulate materials has increased, and work has been started in new areas of investigation concerning problems of heat release in reactors and of reactor control.

Reactant Depletion in Isothermal Reactors

Studies of isothermal reactors have been concerned with effects of mixing in the presence of nonuniform dose rate distributions and nonuniform residence time distributions. These investigations may be divided into two categories, depending on the substance giving rise to the mixing effect. Thus mixing effects may arise from move-

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ment of reactant or from movement of reactive intermediates.

When movement of reactant is the basis of an effect of mixing, the effect is referred to as one due to reactant depletion. Reactant depletion gives rise to no observable change in rate with degree of mixing at small conversions. However, at high conversions an effect may be found. Calculations performed during the past year for single-step reactions in a number of combinations of reactor geometries and flow states have suggested some of the features of the reactant depletion problem. For photosensitized reactions conducted in a batch slab reactor or in a continuous laminar flow tubular reactor, the introduction of rapid mixing in the direction of radiation attenuation was found to result in increased conversion at a given average contact time, the magnitude of the increase being largest at intermediate conversions and increasing with optical thickness. On the other hand, for a single-step reaction following Beer-Lambert law absorption with the same combinations of reactor geometry and flow state, no mixing effect was found in the batch slab reactor, and a small effect which decreased with optical thickness was found in the flow reactor.

An attempt was made to generalize the results for the photosensitized reaction without solving in detail a large number of problems associated with combinations of different rate laws, radiation attenuation modes, reactor geometries, and flow states. Reactions were considered that proceeded at a local rate proportional to the product of a nonnegative power of the reactant concentration and a well-behaved function of position. Reactor types assumed were batch reactors of arbitrary geometry and flow reactors with arbitrary flow cross sections and arbitrary velocity distributions over these sections. For these circumstances the existence and direction of effects of mixing and their effect on the conversion history were examined. It was shown mathematically, mainly through the use of the Hölder inequality, that in the absence of nonuniformities no mixing effect exists and that in the presence of nonuniformities a mixing effect generally exists. Furthermore, in the latter instance the effect of mixing is to produce an increase in conversion as a function of time over that found in the absence of mixing. The model for which these conclusions were drawn is an idealization for a number of photochemical, radiation chemical, catalytic, and thermal reactions, and thus

constitutes a reference point for the examination of mixing effects in many chemical fields.

R. FELDER, N. REISS,* L. SHENDALMAN**

Experimental study of mixing effects arising from reactant depletion is in progress with use of three radiations: β particles, ultraviolet light, and γ rays. One of the main practical consequences of this work concerns dosimetry, and the particular problems under study, which are described below, are all framed in terms of this subject.

Beta Reactor. The reactant depletion problem with highly attenuated radiations is well exemplified by the oxidation of ferrous sulfate in sulfuric acid solution as brought about by β radiation. Apparatus for the study of this problem was constructed during the year. The line source shown in Figure 17 was procured from the 3M Company. It contains 3M microspheres loaded with ≈ 20 Ci of $\text{Sr}^{90}\text{-Y}^{90}$ distributed over a 30-cm length. The microspheres are contained within a single 0.096-in.-diam stainless steel tube with 3-mil wall thickness. In use the source is located in a thin glass well (0.2-mm wall thickness) on the center line of the annular flow reactor also shown in Figure 17. The source and reactor are incorporated into a once-through flow system (Figure 18) made of glass and Tygon tubing. The reactor is located within a shielded cell (Figure 19) along with a source pig. Other parts of the flow system are located outside the cell (to the left of the cell in Figure 19).

Objectives of the experiment conducted in this apparatus are to examine the problems of dosimetry in a flow reactor of the type described and to determine the mean dose rate in such a reactor.

As background for the experimental work, calculations were made of the product concentration vs mean absorbed dose, taking into account the features of the reactant depletion problem. The kinetics expressions used were those of Allen and Rothschild [*Radiation Res.* **7**, 591 (1957)] for the air-saturated system. These expressions were embodied in the equations for the flow reactor with a fully developed laminar velocity profile and with the absorbed dose rate distribution predicted by Loevinger's empirical equations [R. LOEVINGER, *Radiology* **66**, 55 (1956); J. SILVERMAN, in *Large Radiation Sources in Industry*, Vol. 1, p. 31, IAEA, Vienna, 1960]. The equations were formulated

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Figure 18. Once-through flow system for beta reactor flow experiment.

Figure 19. Shielded cell and associated equipment for beta reactor flow experiment.

for two extreme states of radial diffusion or mixing: perfect mixing (PM) and no mixing (NM). Numerical solutions were obtained.

A graph of the calculated results is shown in Figure 20. The PM curve is valid for all radial reactor thicknesses for the abscissa chosen, and it corresponds effectively to plug flow and a uniform dose rate equal to the mean dose rate. It exhibits the well-defined break at the point of oxygen depletion normally found in experiments with uniform residence time and dose rate throughout the reaction volume. The two solid NM curves are for radial reactor thicknesses of 2 and 6 mm. The dashed curve is the NM curve for the 6-mm annulus with a small amount of bremsstrahlung present. These curves show the expected characteristics of the reactant depletion problem – no effect at low conversions, a maximum effect at intermediate conversions, and an increasing effect with increasing optical thickness.

The NM curves cannot generally be calculated with accuracy, since they are dependent upon an independent knowledge of the velocity and dose rate distributions. The PM curve depends only on mean values of these distributions and so can be calculated with confidence. Accurate dosimetry in a flow system consists then in determining the initial slope of the product concentration vs the contact time curve. This is identical to the slope of the PM curve regardless of the nature of the velocity and dose rate distributions.

Figure 20. Calculated performance of beta reactor for ferrous sulfate oxidation.

The first set of values of product concentration as a function of flow rate in the laminar region has been obtained in a reactor with a 6-mm annulus by using the standard aerated Fricke dosimeter solution as reactant. The data are tentative because more effective flow and temperature controls are required; nevertheless they agree very well with the calculations shown in Figure 20 for no mixing and the presence of bremsstrahlung. The mean dose rate based on the initial slope is 120,000 rads/hr. For a source of 20 Ci this corresponds to a source utilization efficiency of 22%.

This work will be continued with refined apparatus in both the laminar and turbulent flow regimes, with reactors of other dimensions and types, and with other flow arrangements including recirculation.

C. DAVIS, J. EICHACKER,
A. MULLER, M. ROTHBART, R. ZAVODOSKI*

Ultraviolet Light and Gamma Reactors. Preparations are being made to study two other reactant depletion problems. In one case, an inquiry will be made into the effect of mixing in optically thick layers of potassium ferrioxalate actinometer solution. As mentioned earlier, no mixing effect is to be expected on theoretical grounds if the reaction follows Beer-Lambert law absorption. In additional calculations supporting this work, solutions are being sought for the kinetic equations for photolysis of a complex in equilibrium with its components. An apparatus for the experiments is being constructed.

The other reactant depletion problem concerns dosimetry and reactor performance in a continuous-flow stirred tank reactor. A Co^{60} γ source will be used to initiate the Fricke dosimeter reaction. Mixing studies in the absence of reaction have been conducted in a number of 6-in.-diam $\times$ 12-in.-high stirred glass reactors, each having a well on the axis for a line source. Mixing studies have been carried out with use of a dye tracer technique. The purpose of these experiments was to permit selection of impeller designs and locations, impeller speeds, and through-flow rates that correspond essentially to perfect mixing throughout the reactor volume. These will be the conditions used in the presence of reaction. Upon selection of a satisfactory mixer design a once-through flow system will be set up for dosimetry and reactor performance studies.

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Mixing Effects in Chain Reactions

Mixing effects may be found in optically thick isothermal reactors even at low conversions if the local reaction rate is proportional to the concentration of long-lived intermediates which disappear via mutual reaction, as in chain reactions and polymerizations. Several topics related to mixing effects in chain reactions are under investigation.

Effects of Mixing on a Nonuniformly Initiated Polymerization. Experiments were continued on the photopolymerization of methyl methacrylate using the partial illumination technique. Development and construction of the apparatus were described in last year's report. During the past year, measurements were made of the rate of the direct photoinitiated polymerization as a function of stirrer speed in a partially illuminated dilatometric cell. The fraction of the cell that was illuminated, defined as $1/\tau$, was the principal parameter in the experiments. Measurements were made in each of two cells over the stirrer speed range 0 to 1000 rpm at values of τ of 1, 2.2, and 50. The data for one cell are shown in Figure 21. The ordinate is the rate at a given τ and stirrer speed, divided by the rate at the same τ and 0 rpm. The abscissa is the stirrer speed on a logarithmic scale. The S-shaped form of the curves is expected on theoretical grounds, although, because of the complex nature of the mixing process, the curves are difficult to predict in detail. The

Figure 21. Rate of direct photoinitiated polymerization of methyl methacrylate in a partially illuminated cell as a function of stirrer speed. The ordinate is the rate divided by the rate at zero rpm. The fraction of the cell illuminated is $1/\tau$. Each set of data points identified by a given symbol was obtained with a single monomer charge.

high speed limit is readily predictable provided that the absorbed light intensity is constant throughout the illuminated portion of the vessel. Under these circumstances the high speed limit is equal to $\tau^{1/2}$. Theory and experiment are in good agreement for $\tau=2.2$. For $\tau=50$, the limiting rate was not reached. No variation of rate with rpm should have been found for $\tau=1$, although a 15% increase was measured which was presumably due to nonuniformities in the incident beam and/or strong absorption at some light wavelengths. The data for the two cells are in agreement for $\tau=1$ and $\tau=2.2$. At $\tau=50$, for reasons not yet understood, there was considerably greater scatter in the data for the second cell, although the same form of curve was indicated.

The data shown in Figure 21 were obtained in experiments in which rates were measured at several speeds over the complete rpm range with each monomer charge. These data were found to depend on the direction of variation of stirrer speed. With one exception all the runs shown in Figure 21 were started at the maximum speed and then run at several successively lower speeds. In the run indicated by the diamond-shaped symbols, stirrer speed was increased progressively from 0 rpm to the maximum. The curve defined by this run is higher at low speeds and lower at high speeds than the solid curve which represents the other runs. This difference is probably due to the compounding of the effects of stirrer speed and viscosity. Viscosity evidently changes rapidly with conversion even at small conversions. (Conversion in all runs did not exceed 1%.) In experiments now in progress, data are being obtained for a single speed per monomer charge. The rate is measured as a function of time and extrapolated to zero time to obtain the rate at zero conversion.

J. EICHACKER, L. YEMIN

Effects of Mixing on Molecular Weight Distributions. In support of the proposed experimental work described immediately above, and as a general inquiry on the subject, a series of calculations of effects of mixing on molecular weight distributions in nonuniformly initiated addition polymerizations has been undertaken. Several types of initiation are being considered: direct photoinitiation, photodissociation of catalyst, thermal dissociation of catalyst, and radiation initiation. Other steps in the mechanism under consideration include propagation, termination by combination and disproportionation, and transfer to

monomer and solvent. Programs are being written for batch reactors and continuous-flow stirred reactors.

C. BENKOVITZ,* H. CHEN**

Pulsed Gamma Source Characterization. An experimental characterization of the wave form obtainable from a type of pulsed γ source has been carried out. In concept a strip source of Co^{60} is conformed to the shape of a segment of a circle and mounted on the periphery of a lead disk. The disk is rotated adjacent to an aperture in a lead wall, and pulses of γ radiation pass through the aperture. This arrangement of source and aperture was mocked up and the pulse wave form was measured with a silicon solar cell dosimeter. The wave form was found to be trapezoidal with curved corners. Calculations will now be made to determine its usefulness in rotating sector determinations of radical lifetime in chain reactions and polymerizations.

P. FALLON, A. MULLER

Heat Release and Reactor Control Problems

Work has been started on several problems involving radiation chemical reaction systems with significant heat release rates. In one case, thermal stress problems encountered during radiation polymerization of monomer-impregnated solids such as wood and concrete are being examined. In another the stability criteria for exothermic photo-initiated reactions with positive temperature coefficients are being established. In a third, the feasibility of controlling an inherently unstable continuous-flow stirred radiation chemical reactor is under study. Results on these problems are not yet available.

H. CHEN, M. ROTHBART,
L. SHENDALMAN

Radiation Treatment of Liquids and Particulate Materials

In applications such as extracorporeal irradiation of blood and radiation disinfestation of grain in bulk flow, equipment design problems have certain similarities to those in radiation chemical reactors. Radiation attenuation and a residence time distribution will exist in the equipment, and the effect of these nonuniformities on the index of performance must be predicted. In the two applications cited the index of performance is absorbed dose range rather than reaction rate, yield, or product distribution. Prediction of this index con-

stitutes a formidable problem and requires a knowledge of target paths as well as velocity distributions and dose rate distributions. As a start on this problem, the cumulative dose distribution in a liquid treated in a laminar-flow tubular reactor with outside radiation has been calculated. As expected, the distribution was found to be broad. It started at a minimum dose, corresponding to the minimum value of the quotient of the local dose rate divided by the local velocity, and it continued to the infinite dose found both at the tube wall, where an infinite residence time exists, and at the tube center, where the dose rate is infinite. The breadth of the distribution decreased with decreasing absorption coefficient. Calculations will be continued with emphasis on an annular-shaped irradiator and with investigation of the influence of a radial component of the target motion.

The effectiveness of radiation treatment of biological systems can sometimes be characterized by a rate law, as in the inactivation of bacteria. When this is the case the radiation treatment problem is simplified considerably. An example is the MISER (Microbiological Inhibition Systems Employing Radiation) scheme. Equations have been derived for recirculating MISER systems and have been applied by the Atlantic Research Corp. in economic evaluations (see NYO-3736-2).

R. FELDER, F. HILL

Bulk Grain Irradiator. In connection with the dose distribution problem described above, a study of calibration problems associated with the Bulk Grain Irradiator (BGI) in Savannah, Ga., has been undertaken. In the BGI it is desirable and may be required to measure the absorbed dose distribution. It is thought that this might be done through the use of a particulate tracer-dosimeter in which the particle is both tracer and dosimeter. A suitable device insofar as dosimetric properties are concerned is the Bausch and Lomb borosilicate glass dosimeter. It can be made small, roughly twice the size of a grain of wheat, so that it will be readily recoverable from bulk grain, and is adequately sensitive in the dose range of interest (5000 to 50,000 rads). A kit consisting of spectrophotometric sample holders and dosimeters has been prepared for possible use at the BGI. The tracer properties and fragility of these particles remain to be investigated.

C. DAVIS, A. MULLER

Low Dose Dosimeters. In connection with the general problem of low dose measurement, and

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especially in relation to the BGI calibration, some effort has been devoted to the development of physically small low dose dosimeters. Potential dosimeters of interest are those that are convenient to use in the sense that the dose measurement is a rapid physical one. Two types have been studied. The first, the UVT Lucite dosimeter developed for the megarad range, can be used to measure doses of 20,000 rads to within 10% if it is used in sufficient quantity to get good statistics. The second is a new type called the quartz dosimeter, in which thin quartz plates about twice the size of wheat grains are sensitized by a dose of up to 10^9 rads of Co^{60} γ radiation. This type of glass dosimeter differs from others in that the sensitization is produced by the use of a large γ dose rather

than a high-Z additive. After the sensitizing dose is imparted, the dosimeters are heated to 400°C and held there for several hours. This treatment releases electrons from the color centers but does not destroy the centers themselves. The samples color linearly at $215\text{ m}\mu$ at the rate of 0.03 absorbance unit change per kilorad up to 50,000 rads. This rate is readily measurable and is nearly an order of magnitude greater than the rate of coloring in UVT Lucite. The coloring rate cited is for Infrasil quartz. Lower rates were found for other, less pure grades of quartz. In future work the optimum combination of sensitizing dose and annealing temperature will be sought. Alkali halide crystals will also be tested as dosimeters of this type.

J. EICHACKER, A. MULLER

Figure 22. Rectangular neutron pulse starting to enter the slab, and eight iterations after.

TIME-DEPENDENT TRANSPORT THEORY CALCULATION METHOD

Work is continuing on a method for calculating time-dependent transport problems whose solution in as much detail as desired has not been very practical. As discussed more completely in the last annual report, the method consists of literally following the motion of the elements of the phase space of the problem being studied, with use of a high-speed digital computer to keep track of the additions and subtractions to the element due to interactions and its deformation as time increases. To date, results [M. TAVEL AND M. ZUCKER, *Trans. Am. Nucl. Soc.* **10**, 213 (1967)] have been published on neutron pulses originating in infinite, semi-

infinite, and finite media and in vacua adjacent to finite and semi-infinite media. A planar symmetry, infinite mass scatterers with isotropic scattering cross sections, and a speed homogeneous to within some Δv , were assumed.

A typical result is illustrated in Figures 22 and 23. The situation here is that of a pulse of neutrons normally incident on a slab of finite thickness, with vacuum on either side. The pulse is initially rectangular, i.e., uniform in density over a finite interval and zero everywhere else. The neutrons are assumed to have a speed inhomogeneity of $(\Delta v/v) = 5\%$, and their spatial extent is $(\Delta x/v\Delta t)$, where Δx represents the element of length in phase space and Δt is the time increment between successive determinations of the density of neutrons.

Figure 23. The same pulse as in Figure 22, at time intervals 10 to 16 after the initial time.

The scattering cross section of the scattering centers making up the slab is such that $\exp(-\sigma v \Delta t) = 0.9$ (where σ is the density of scatterers multiplied by the integrated cross section); i.e., 0.1 of the uncollided beam will collide during any given time step. Each member of the family of curves represents the logarithm of the density of neutrons as a function of distance along the normal direction to the slab at a particular time, $t = n\Delta t$ (n is an integer), after the initial distribution existed. At time $t = 0$, the right edge of the neutron pulse bordered the left edge of the slab (boundaries demarcated by two vertical parallel lines). The first 9 time steps are shown after $t = 0$. In Figure 23, the first time step shown is the step after the last one in Figure 22. In the two figures are shown the time evolution of the neutron density as it impinges on the slab, the attenuation of the uncollided flux in its passage through the slab, and its emergence from the extreme right edge. Also shown are the "reflected" component to the left of the slab, "buildup" within the slab (a local density greater than the density of the initial pulse), and an approach to a crude sinusoid steady-state form for the density within the slab as time increases. Besides these qualitative features, there are the actual values of the density as a function of time and position, calculated in far greater numbers and in less time than is possible with any other known method of calculation. The CDC 6600 running time to generate this considerable amount of data is of the order of only 5 min.

The present effort is to improve the calculational scheme so that it may include nonisotropic though still elastic scattering cross sections, fission, and absorption. When this program is completed, finite mass scatterers and several energy groups will be included. It will then be possible to handle the whole range of neutron transport problems with this technique. M. ZUCKER, M. TAVEL

MAGNETOHYDRODYNAMICS EVALUATION

Graphite and the refractory metals and alloys appear to be the only container materials usable for MHD applications in the temperature range 2500° to 4000°F. An investigation was therefore conducted by the General Electric Company's Nuclear Materials and Propulsion Operation in cooperation with BNL to determine the stability of several refractories in pure nitrogen at 3500°F. Screening tests were conducted in static gas for periods up to 1000 hr with W, Mo, Re, W-25%

Re, W-30% Re-30% Mo, and Mo-50% Re. Specimens of W-UO₂-ThO₂ clad with W-30% Re-30% Mo were also tested. Visually, no detrimental effects were observed on any specimens. On the basis of metallographic examinations, weight changes, hardness, and chemical analysis, it was concluded that Re and Mo are stable in pure nitrogen for 1000 hr at 3500°F and do not absorb nitrogen to any extent, while W may be mildly affected by nitrogen. H. SUSSKIND

CLOSED-CYCLE NONEQUILIBRIUM NUCLEAR MAGNETOHYDRODYNAMICS

Because of budgetary restrictions, only limited chemical physics work continues on the investigation of nonequilibrium electrical conductivity in a Cs-seeded, noble gas plasma by means of collisional ionization of Cs by metastable N₂ molecules. In the past year emphasis has been on the reactions of metastable molecules produced in a high-power, high-frequency rf discharge.

The electrical conductivity of Na-seeded 1 atm N₂ has been measured as 0.3 mho/m, 100 msec after rf excitation ceases. This corresponds to an electron density of $\approx 3 \times 10^{12}/\text{cm}^3$. Similar electron densities have been observed in 30% N₂-70% Ar mixtures seeded with Na. Small admixtures of O₂ reduce conductivity to zero. Although simultaneous temperature measurements have not yet been made, temperature measurements on similar plasmas (and the O₂ effect) indicate that the conductivity is nonequilibrium.

Simultaneous temperature and luminosity measurements show $\approx 10^{16}/\text{cm}^3\text{-sec}$ light quanta at temperatures of 1000 to 1500°K where thermal excitation would require temperatures $> 3000^\circ\text{K}$. This excitation rate is of the order necessary to maintain the observed conductivity.

The Na seeding was obtained by flow of the gas past a solid Na chip. Seeding by a gas with a lower ionization potential (Cs) will probably increase electron density and conductivity.

Spectrographs of the afterglow in N₂ show a line spectrum characteristic of the electrode material (e.g., Pt or Cu) and impurities present (e.g., Na, Fe, and Ca). Spectral intensity measurements with a densitometer indicate that the most intense lines originate from levels 3 to 4 eV above the ground state. The energy of this transition matches the energy of the most probable radiative transition in the metastable N₂ molecule.

BALL LIGHTNING

In the course of experiments with the rf-induced plasmas mentioned above, it became evident that the long-lived plasmas ($\frac{1}{2}$ to 1 sec after rf excitation ceased) bore a startling resemblance to natural ball lightning, a phenomenon for which there has been no satisfactory explanation.

Both N_2 and O_2 have very long-lived (≥ 10 sec) metastable states, and considerable energy can be stored in either gas or mixtures thereof (e.g., air). In studies of the luminous emission of air and O_2 , it was found that ≈ 80 W was initially emitted from an air luminosity ≈ 5 in. in diameter, decaying exponentially with a time constant of 0.3 sec, and 160 W from an O_2 luminosity of the same dimensions and time constants. In every aspect but lifetime they matched the reported characteristics of natural ball lightning. For the latter, an average lifetime of 3 to 4 sec is reported, with some events lasting 10 to 20 sec. Theoretical analysis shows that the observed dc electric field in the vicinity of a lightning stroke (1000 to 2000 V/cm) is sufficient to prolong the life of the luminosity and generate new metastable molecules to replace those destroyed.

Simultaneous luminosity-temperature measurements show the temperature of the radiating air to be 2000 to 2500°K. The equilibrium radiation at these temperatures is several orders of magnitude below the observed values.

Spectral analyses in O_2 and air show that the majority of radiation comes from the $CO_2^* \rightarrow CO_2 + h\nu$ (continuum) and O_2 Schumann-Punge bands. There are some weak lines and some bands (e.g., CuO and PtO) characteristic of the electrode used. Presumably these radiating species are excited by collisions of the second kind from the metastable molecules. There is some NO_2 emission in air but it is considerably less than CO_2 emission. Most ($>60\%$) of the radiant emission occurs in the visible (4000 to 7000 Å) region, with some in the ultraviolet and infrared regions.

J. POWELL, R. DOMISH

ATMOSPHERIC SULFUR POLLUTANTS PROGRAM*

An investigation into the feasibility of utilizing naturally occurring differences in the ratios of the stable isotopes of sulfur as a means of relating atmospheric sulfur to the major sources from

which it originates has been undertaken jointly with the Meteorology Group of the Instrumentation and Health Physics Department and the Analytical Chemistry Group of the Hot Laboratory Division.

The technique involves sampling SO_2 and particulate sulfate in the atmosphere by means of chemically treated filters, converting the sulfur quantitatively into a suitable standardized form, and then determining the isotopic ratios in an isotope ratio mass spectrometer.

Sulfur in terrestrial deposits is composed of four stable isotopes in the approximate proportions S^{32} , 95.1%; S^{33} , 0.74%; S^{34} , 4.2%; and S^{36} , 0.016%. The isotopic composition varies, depending presumably upon the bacterial action operative during the formation of the sulfur deposit, and it is this variation that makes it possible to consider tracing stack plumes by using the natural differences found in fossil fuel from different sources. The ratio of two of these isotopes (S^{32} and S^{34}) varies by about 700 parts in 10,000, and it is possible to distinguish differences of ≈ 2 parts in 10,000.

The constant S^{32}/S^{34} ratio of meteoritic sulfur, 22.210, has been accepted as the standard. The difference between the standard and the ratio in a sample is measured in units of "per mil of S^{34} " (δS^{34} , ‰), and is defined by

$$\delta S^{34} = \left(\frac{22.210}{S^{32}/S^{34} \text{ (sample)}} - 1 \right) 1000.$$

A sample having a higher abundance of S^{34} than the standard would have a positive δS^{34} , or plus per mil value; one with a lower abundance would have a negative δS^{34} , or minus per mil value.

There are two significant advantages in using the S^{32}/S^{34} ratio as a tracer; first, SO_2 itself can actually be used, rather than simulation of SO_2 by another tracer; and second, there may in some circumstances be adequate differences between the ratios in fuels currently in use to permit experiments to be done with no tracer added to the system.

To utilize the method, it is necessary to have a sampling system capable of extracting relatively large amounts of SO_2 (or other sulfur compounds) from the atmosphere at low concentrations, a reliable chemical separation and purification system, and a ratio mass spectrometer designed specifically to accept small volume samples.

A field system for the collection of SO_2 samples on a routine basis has been worked out, the ratio

*Partially supported by the U.S. Public Health Service.

spectrometer has been ordered, and a chemical procedure developed that will produce satisfactory samples.

Based on the method of Huygen [*Anal. Chim. Acta* **28**, 349-60 (1963)], a system has been established that uses either Whatman #41 or "Fast Flow" filter paper impregnated with potassium hydroxide in a standard high-volume sampler. The air flow rates obtained range from 0.6 to >2.0 m³/min. It is surprising that SO₂ collection efficiency remains high at these high flow rates, but this has been carefully verified. Efficiencies of $\geq 95\%$ are being obtained, as is required if a sampling system is not to affect the existing ratios of S³²/S³⁴ by fractionation in the collection process. It is possible to collect samples of at least 1 mg, the minimum needed for analysis, in 1 hr in an SO₂ concentration of 0.01 ppm.

Field sampling will include airborne operation, and the technique has been adapted for this purpose. This involves the use of a standard high-volume sampler with augmentation of the flow rate by a ram-air intake fitted to the window aperture of the aircraft. An impregnated 8 × 10-in. filter sheet will be used with a quick-change mount as the sampling medium.

Also under development is a filter pack designed to separate SO₂, SO₃, and particulates containing sulfate or adsorbed SO₂. The purpose of this system is to assist in the study of the conversion of SO₂ to other compounds during the dispersion of the plume.

The filter papers from the samplers are processed by washing with water, collecting the sulfur in solution as sulfite, oxidizing to sulfate, and precipitating as BaSO₄. The sulfate is reduced to H₂S, converted to CdS, metathesized to Ag₂S, and oxidized to SO₂ in a stream of oxygen of constant O¹⁸/O¹⁶ ratio. After purification, the SO₂ is ready for introduction into the mass spectrometer for measurement. The necessary equipment has been fabricated, assembled, and tested. Pending delivery and installation of the mass spectrometer now on order, mass ratio determinations have been carried out by two laboratories specializing in this type of analysis, those of Prof. Thode of McMaster University and Prof. Jensen of the University of Utah. Results obtained so far are summarized in Table 14. Analyses have been run on samples of fuel, both coal and oil, and of sulfur from different sources, for possible use as tracer material. The accumulation of background data

Source of sample	S ³² /S ³⁴ , $\delta S^{34}_{0/00}$
Possible sulfur tracers	
1. Cylinder SO ₂ , No. 1	-5.1
2. Cylinder SO ₂ , No. 2	+5.5
3. Cylinder SO ₂ , Virginia Chemical Co., No. 3	-7.7
4. Cylinder SO ₂ , can-o-gas, No. 4	+5.4
5. H ₂ SO ₄ from Imperial Chemical Industries	+10.6
6. Crude oil, American Oil Co., A	-6.7
7. Crude oil, American Oil Co., B	+2.9
8. Coal, Breaker refuse, A	-5.7
9. Coal, Breaker clean, B	+2.5
10. Elemental sulfur	-5.6
Long Island Lighting Co., Port Jefferson Plant	
11. Fuel oil	+4.5
12. Stack breeching	+5.8
13. Plume, ½ mile from stack (airborne sampler)	+6.0
Stack plumes, airborne sampling	
14. LILCO, Port Jefferson Plant	+5.3
15. Con Ed, Hudson Plant	+5.2
16. Con Ed, East River Plant	+5.3
17. Public Service of New Jersey Plant	+4.6
18. New Haven Plant, downwind of stack	+4.9
19. New Haven Plant, upwind of stack	+5.5
Background samples, ground level	
20. New Haven composite	+8.0
21. New York City, 121st Street	+6.0
22. New York City, New York University	+5.5
23. New York City, LaGuardia Airport	+5.5
24. New York City, Samuel Gompers High School	+3.9

on sulfur in the atmosphere has begun, with samples taken in New York City, New Haven, and the vicinity of BNL. Samples have also been taken aloft in the plumes from power plant stacks. All the atmospheric samples run are in the +4 to +8 range, while several fuel and chemical sources have negative ratios large enough to indicate that successful experiments can be conducted.

There are several possible ways in which the isotope ratio tracer can be utilized. It seems probable that some smaller municipal areas may have one or two large sources burning fuel (e.g., coal) having S³²/S³⁴ ratios quite different from that of the fuel used for home and apartment heating. Where this is true it should be possible to evaluate

the specific contributions of the two types of source with relative ease, since it should be possible to detect 1 part of stack SO_2 in 50 parts of background SO_2 .

More complex municipal areas may have wide variation in source ratios and strengths, and the course of pollution studies will depend upon the magnitude of variability encountered. If the fluctuations are large, correspondingly large variations in source ratios are implied, and study of the samples in relation to meteorological variables should help in the assessment of the pollution problem in the area. If, on the other hand, the typical city samples are fairly uniform, a single source can be tagged either by the use of a fuel having a $\text{S}^{32}/\text{S}^{34}$ ratio that is markedly different from the background value or by the addition of SO_2 with a sufficiently different ratio to the stack gas.

Finally, the use of a filter pack for sampling should indicate the rate of change of SO_2 from a particular source to SO_3 or sulfates in an atmosphere containing SO_2 and other pollutants from a multiplicity of sources.

Three different areas are to be studied, tall-stack sources being used in each. Samples will be collected simultaneously from stack plumes and fuel being burned, and the pattern of ground-level background will be established over a considerable period of time, including seasonal and diurnal variation. These areas are New York, a large metropolitan complex; New Haven, a compact city with a single large power source; and the Keystone Plant in Western Pennsylvania, a large source in a rural area. R. BALDWIN, L. COHEN, J. FORREST, J. FRIZZOLA, B. MANOWITZ, L. NEWMAN, C. SCARLETT, M. SMITH, M. STEINBERG, W. TUCKER

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Hot Laboratory Division

L.G. STANG JR.

Work that had formerly been reported under the headings Isotope Research and Development and Isotope Production and Development has been reoriented. Henceforth it will be reported under Nuclear and Radiochemical Research on Special Isotopes and Isotope Applications Development. This reorganization reflects a shift in the relative importance of various phases of the isotopes picture now that private industry has finally assumed responsibility for the production of some of the Brookhaven-developed short-lived isotopes of special importance and, as a consequence of which, Brookhaven has for practical purposes withdrawn from the production of all short-lived isotopes except Mg^{28} . The new arrangement permits effort to be devoted on the one hand to the fundamental study of those aspects of nuclear chemistry that are especially pertinent to nuclear engineering problems, and on the other hand to the development of new kinds of applications of isotopes, both without the encumbrance of day-to-day problems that arise in connection with the production and distribution of a product.

Nuclear and Radiochemical Research on Special Isotopes

M. HILLMAN

CHEMICAL EFFECTS OF TELLURIUM ISOMER DECAY

The decay of $\text{Te}^{129m}(\text{VI})$ was investigated under carefully controlled conditions to determine how the relative amounts of the resultant oxidation states are affected by local environment and by the degree of polymerization of the decaying tellurium.

From the results to date it has been concluded that there are formed *at least* three hot atom species, the formation and/or the reaction of which with the medium depend on the *pH*. The formation of two of these species depends on the environ-

ment [i.e., the decay of $\text{Te}^{129m}(\text{IV})$ yields a different distribution of products than does the decay of $\text{Te}^{129m}(\text{VI})$]. This appears to be contrary to the explosion theory that was thought to explain isomeric transitions. However, one species or group of species is easily oxidized by air, and it was found to be independent of whether the source was $\text{Te}(\text{IV})$ or $\text{Te}(\text{VI})$; it may be the part of the product formed by the explosion of the molecule.

No evidence was found for differences in behavior between polymeric $\text{Te}(\text{IV})$ and monomeric $\text{Te}(\text{VI})$.

A. J. WEISS, M. HILLMAN

SZILARD-CHALMERS REACTIONS

In Metallophthalocyanines

The Szilard-Chalmers effect when 14-MeV neutrons bombard hafnium phthalocyanine was studied. Retentions of 8% but no isotope effect were observed in solid targets for $(n,2n)$ reactions on Hf^{174} and Hf^{176} and for the (n,n') reaction on Hf^{180} . No isotope effect was expected if all of the retention is due to displacement of the hafnium in the hafnium phthalocyanine by recoil hafnium atoms, the only type of retention possible, since no activated hafnium atom can have recoil energies small enough to permit primary retention. The recoil energy distributions were calculated and the results for the $\text{Hf}^{174}(n,2n)\text{Hf}^{173}$ reaction are shown in Figure 1.

Isotope effects had previously been noted in the retentions of Zr^{95} vs Zr^{97} and in Hf^{180m} vs Hf^{181} (but not between Hf^{181} and Hf^{175}) in (n,γ) reactions in respective solid phthalocyanines. By noting that the $\text{Zr}^{96}(n,\gamma)\text{Zr}^{97}$ and $\text{Hf}^{180}(n,\gamma)\text{Hf}^{181}$ reactions are identical systems in that the spin changes are both zero, it was possible to calculate the probabilities of the recoil energy distribution for each reaction. The ratios of these probabilities are shown in Figure 2. Our experimentally observed ratio of retentions of $\text{Zr}^{97}/\text{Hf}^{181}$ was 0.34 ± 0.04 , which is very close to the calculated ratio of 0.33 at 10 eV. The closeness of these values is extremely encouraging and seems to indicate the correctness of our

Figure 1. Calculated probabilities of recoil energy of Hf^{173} from the bombardment of Hf^{174} with 14.5-MeV neutrons. Note that the abscissa is in keV and that the probability of recoils of <10 keV is virtually zero. Only ≈ 10 keV are required for breaking bonds.

interpretation that differences in primary retention are due to differences in recoil energy spectra, which, in turn, are due to differences in spin changes in going from the starting material to the product. Even if the energy necessary to break bonds was only 5 eV or as high as 15 eV, the calculated ratios at those energies are 0.31 and 0.36, respectively, and still very close to the experimentally observed results. M. HILLMAN, E. SHIKATA

In Zirconocene and Hafnocene Dichlorides

A study was made of the extent to which certain zirconium and hafnium nuclides incorporated in their biscyclopentadienyl dichloride derivatives remain in their parent chemical form after having undergone radiative neutron capture. Targets were in solid form and in dilute solution in order to distinguish between those events in which there is no bond rupture in the parent molecule and those in which primary recombination (the activated atom rapidly recombines with the residual target molecule) or possibly diffusive recombination occurs. In dilute solution the solvent molecules would be expected to prevent recombination. That is, the results of the solution experiments would be expected to measure true primary retention and

Figure 2. Recoil energy probabilities. — — —, $\text{Zr}^{96}(n,\gamma)\text{Zr}^{97}$; — — —, $\text{Hf}^{180}(n,\gamma)\text{Hf}^{181}$ (1-MeV grid); •, $\text{Hf}^{180}(n,\gamma)\text{Hf}^{181}$ (0.5-MeV grid); ·····, $\text{Zr}^{97}/\text{Hf}^{181}$. The grid refers to the multiples of possible energies used in the calculations. The important point to note is that for energies of ≈ 10 eV, which is the approximate energy required to break bonds, the ratio of recoil energies for $\text{Zr}^{97}/\text{Hf}^{181}$ is 0.33.

the difference between these results and those from solid targets would be expected to measure recombination. The results are shown in Table 1.

R.M.A. HAHNE*

EXCITATION FUNCTIONS

General Calculations

In calculating the evaporation probabilities of heavy particles from nuclides at high excitation energies, a realistic spin-dependent level density relationship is needed. Therefore we set out to write a computer program that would calculate level densities from first principles using a single particle model. The first program lacked nucleon-pairing corrections, which turned out to be necessary. A number of devices were used in an effort to introduce realistic pairing corrections into the calculations. Although no realistic correction has yet been found, other modifications remain to be tried.

M. HILLMAN, D. DAVIS**

*Visiting Scientist.

**Summer student.

Table 1

Retentions of Hafnium and Zirconium Nuclides Under Various Conditions (in percent)^a

Product nuclide	Solid zirconocene dichloride	Zirconocene dichloride solution	Solid hafnocene dichloride	Hafnocene dichloride solution
Hf ¹⁸¹	23.1	7.38 ^b	21.4	6.93
Hf ^{180m}	58.7 ^b	28.2 ^b	56.5	27.2
Zr ⁹⁷	18.2	2.38	—	—
Zr ⁹⁵	23.9	4.20	—	—

^aNote in particular that the retention of Hf^{180m} is high, both on an absolute basis and relative to the other nuclides studied, being almost 2½ times that of Hf¹⁸¹. The retention of Hf^{180m} in solution is about half that in the solid, but still high, while the retentions of the other three nuclides in solution are 10 to 30% of the respective values in the solid. The results for the behavior of hafnium nuclides in the solid and solutions of hafnocene dichloride agree remarkably well with the results of the behavior of hafnium impurity in zirconocene dichloride.

^bThese results are based on hafnium as an impurity in zirconocene dichloride.

Figure 3. Excitation functions for Na²⁴ and Be⁷ produced from alpha-particle bombardment of aluminum.

Alpha Particles on Calcium-48

Monte Carlo evaporation calculations were performed for all ($\alpha, \alpha n$) reactions for which excitation functions are in the literature in an attempt to correlate differences among targets. With some ex-

Figure 4. Excitation function for the Ni⁵⁸($\alpha, \alpha p n$)Co⁵⁶ reaction. The high energy tail is due in part to production of Co⁵⁶ from Ni⁶⁰, but this reaction is probably negligible below ≈ 58 MeV.

ceptions, calculated yields at the maxima were too high for the neutron-deficient target nuclides and too low for the neutron-excess target nuclides. In most cases prediction of the position of the maxima and of the threshold energy agreed reasonably well with measured values. Generally, using the parameters chosen, the evaporation theory seems

increasingly unable to predict the higher yields of (α, n) products as one goes to neutron excess targets. An increasing contribution from a direct-interaction mechanism to the over-all observed yield may be a factor.

B. GORDON

Alpha Particles on Aluminum-27

Reactions of ≤ 80 -MeV alpha particles on aluminum were studied for a number of reasons. The higher energy alphas give (α, xp) reactions, on which practically nothing appears in the literature. At the 40-MeV limit of present knowledge, all the known excitation functions between alpha particles and aluminum are still rising steeply, and not even the shapes are well known. Such reactions yield, among other things, Be^7 and Na^{24} , whose formation may be regarded as the "fission" of a very small (compound) nuclide, P^{31} , about which event little is known.

The most recently determined excitation functions for the production of Na^{24} and Be^7 from alpha bombardment of aluminum are shown in Figure 3. Note that any Be^7 from the $\text{Al}^{27}(\alpha, \text{Be}^7)\text{Na}^{24}$ reaction would also contribute to the Na^{24} yield and yet the measured yield of Be^7 is a very small fraction of that of Na^{24} .

These excitation functions were monitored by several groups of nickel foils interspersed among the aluminum foils in such a way as to measure forward and backward recoils. The results of these measurements are shown in Figure 4.

B. GORDON

TERNARY FISSION

Three-parameter triple-coincidence counting equipment, previously used at the University of Florida for studying ternary fission by simultaneous detection of the three fission fragments, was set up and successfully tested using the $\text{U}^{235} + n \rightarrow \text{U}^{236*}$ system, which yielded events similar to those previously recorded. Separate target foils of Pu^{239} and Pu^{241} are being used to study ternary fission in these two nuclides.

Inasmuch as an unaccountably large amount of Si^{32} has been observed in fallout and because the light mass peak from earlier work on ternary fission appeared to be 30-32, experiments have been undertaken to isolate Si^{32} and P^{32} from an old fuel plate. For this purpose a radiochemical scheme is being developed that will effect a good exchange of the desired nuclides with their respective carriers.

M. MUGA

TECHNETIUM CHEMISTRY

A study of the lower oxidation states of technetium indicated that when pertechnetate solutions in phosphoric acid are reduced by Fe^{+2} , a pink species of Tc is formed at pH 3. This changes reversibly to a blue species when the pH is reduced to 1. However, the concentration ratio of Fe^{+2} to TcO_4^- is at least twice stoichiometric. Attempts to reduce the pertechnetate quantitatively were unsuccessful, nor has it yet been possible to determine the valence of Tc in these species by back-titrating the Fe^{+3} produced during the reduction.

M. RAUSCHER, B. GORDON, M. GREENE

SYNTHESIS OF TRANSPLUTONIC NUCLIDES BY EPITHERMAL NEUTRONS

Correlations of fission and capture cross sections for thermal and epithermal neutrons indicate that epithermal capture cross sections are higher than the thermal cross sections and that the ratio of capture cross section to fission cross section is much higher for epithermal neutrons than for thermal neutrons (Unpublished memo, A. Prince to S. Pearlstein, January 12, 1967). To the extent that this is true, a high epithermal flux reactor would be superior to existing facilities for synthesizing transplutonic nuclides.

In a preliminary experiment to shed further light on this theory, a sample of Cf^{252} was irradiated in the HFBR. The irradiation was expected to produce sufficient Cf^{254} in the sample to increase by 25% its neutron activity (from spontaneous fission). The actual increase was 2.4%, an order of magnitude lower. However, this does not negate the predicted cross sections, because there was considerable scatter of known cross sections about the empirical curve. What it does indicate is the improbability of gaining any significant information from single individual experiments and the desirability of a more intensive series of measurements of the unknown cross sections. A program to do this has been proposed.

M. HILLMAN, B. GORDON

Isotope Applications Development

P. RICHARDS

TELLURIUM-125m

Tellurium-125m (58-day half-life) has potential applications where a low-energy photon emitter is

Figure 5. The effect of time of standing at the labeling pH and of the amount of albumin present on the yield of labeling human serum albumin with Tc^{99m} .

Figure 6. Gel filtration behavior of various species involved in the labeling of human serum albumin (HSA) with Tc^{99m} . The percent of total activity added is shown as a function of amount of eluant required to leach the activity off a Sephadex G-25 column. Curve A shows that I^{131} -labeled HSA appears in the 10th to 14th milliliter of eluant. The similarity of curve B to curve A indicates that Tc^{99m} -labeled HSA behaves exactly as does I^{131} -labeled HSA; this shows that in the procedure used, the technetium activity does bind to the HSA. Ascorbic acid and iron, two reactants involved in reducing the technetium during the labeling of HSA with Tc^{99m} , when tagged with C^{14} and Fe^{59} , respectively, are shown by curves C and D to remain associated with each other, presumably as a complex, and neither remains with the labeled HSA. Unreacted pertechnetate ion appears in still a third fraction (38th to 44th ml) as shown in curve B.

needed. Examples include uses in transmission scanning, as a therapeutic source for interstitial implantation, as a source for autoradiographic studies, and for the preparation of labeled compounds for possible other scanning studies.

Initial efforts were bent toward preparing an Sb^{125} (2.6-year half-life) source of the shorter-lived Te^{125m} and devising methods of separating the latter from the former and of each from the Sn^{125} and (enriched) Sn^{124} precursors. For both purposes electroplating was shown to be satisfactory and superior to ion exchange or solvent extraction. Products free of radioactive contamination were obtained in yields of 78 to 99%.

Millicurie amounts of Te^{125m} were prepared for collaborative studies and evaluation at the Argonne Cancer Research Hospital and the Brookhaven Medical Research Center.

Tc^{99m} -LABELED MATERIALS

Incorporating an element into a complex or a compound invariably alters the biological behavior of that element, although it may or may not alter the behavior of the host molecule. Thus, when the element is a particular nuclide having desirable radiation characteristics, such incorporation provides a means of delivering the nuclide to a new site, or of delivering it by a new route, or with different kinetics; each of these changes offers the possibility of an entirely new set of isotope applications, extending the utility of isotopes in the same way as does the discovery of new isotopes. For example, our development of a Tc^{99m} -labeled colloid, which, when used with appropriate scintillation scanning apparatus permits visualization of the liver, spleen, and functioning bone marrow distribution, was a major cause of the mushrooming demand for this isotope; in the same manner, our development of a method of labeling the iron-ascorbic acid complex with Tc^{99m} has provided a potentially useful means for studying renal function and visualizing the kidneys.

Human Serum Albumin

Further improvements have been made on our method for preparing high specific activity Tc^{99m} -labeled human serum albumin (HSA), which, with suitable scanning equipment, can be used to visualize body blood pools such as the heart or the placenta. The changes improve the product by eliminating other salts, reducing the product

volume, simplifying the labeling procedure by eliminating unnecessary steps, and defining more precisely the conditions under which the others must be performed. For example, the length of time during which the albumin solution is maintained at the labeling pH was found to have an important effect on the final labeling yield (Figure 5).

A gel filtration technique employing Sephadex G-25 to separate the reactants and products into

different fractions was used to show that Tc^{99m} -labeled HSA is a true complex with the desired radioactivity firmly bound to the HSA (Figure 6).

Calcium Diethylene Triamine Pentaacetic Acid (DTPA)

A method was developed for labeling with Tc^{99m} the trisodium salt of calcium diethylene triamine pentaacetic acid (DTPA). DTPA is frequently used for removing heavy metals from the body by forming a chelate, which is then excreted. Preliminary studies with animals at the Brookhaven Medical Research Center indicate that the Tc^{99m} -labeled material may be useful in renal function studies. It may also be useful in renal scanning and in brain scanning.

The method involves reduction of the radioactive pertechnetate ion with Fe^{+2} in HCl in the presence of calcium DTPA. When the pH is raised to ≈ 3.0 , 85 to 90% of the Tc^{99m} is rapidly complexed. After binding, the pH may be raised to a level suitable for intravenous administration. As was done with HSA, a gel filtration technique was used to show that the Tc^{99m} activity is indeed bonded to the DTPA; the results, which are required by the Federal Food and Drug Administration prior to issuing a license for human use, were identical to those obtained with paper strip chromatography and are shown in Figure 7.

Colloids

In most scanning studies using labeled colloids, a major portion of the administered dose is taken up by the liver, smaller amounts being deposited in the spleen and bone marrow, thus making visualization of the bone marrow distribution difficult. Even a small decrease in the fraction of radioactivity going to the liver might greatly enhance the visualization of the bone marrow. The uptake of colloids by these organs and the distribution of the colloid among them is expected to be strongly dependent on the particle size. Microfiltration techniques have established that Tc^{99m} -labeled sulfur colloids prepared with hydrogen sulfide have a particle size at least an order of magnitude smaller than those of similar colloids prepared by the decomposition of sodium thiosulfate, viz., 50 to 100 and 800 to 1000 nm, respectively. These two colloids, being chemically identical, should make excellent tools for studying the effect of particle size on the behavior of the reticuloendothelial system.

Figure 7. Evidence that Tc^{99m} does bind to trisodium calcium diethylene triamine pentaacetate (DTPA). Percent of total entity is plotted as a function of amount of eluant required to leach the entity from Sephadex G-25. Plot A shows $>99\%$ of the Tc^{99m} radioactivity in fractions 9 to 12 and $<0.5\%$ in fractions 21 to 23, where unreacted pertechnetate ion would normally appear (see plot C). Plot B was determined spectrophotometrically and shows the iron-DTPA complex to be in the same fraction with the Tc^{99m} radioactivity. Plot C shows the results, obtained both spectrophotometrically and by radioactive counting, when the iron-DTPA complex was formed in the normal manner but with the Tc^{99m} (as pertechnetate ion) added after instead of before the formation of the complex; the Tc^{99m} radioactivity is now seen in the fractions in which unreacted pertechnetate ion normally appears.

Table 2
Observed and Statistical Values
of the Formation Constants

Reaction	log K (found)	log K (statistical)
$\frac{3}{4} \text{NiCl}_4^{-2} + \frac{1}{4} \text{NiBr}_4^{-2} = \text{NiCl}_3\text{Br}^{-2}$	$0.035 \pm$	0.60
$\frac{1}{2} \text{NiCl}_4^{-2} + \frac{1}{2} \text{NiBr}_4^{-2} = \text{NiCl}_2\text{Br}_2^{-2}$	$0.08 \pm$	0.78
$\frac{1}{4} \text{NiCl}_4^{-2} + \frac{3}{4} \text{NiBr}_4^{-2} = \text{NiClBr}_3^{-2}$	$0.225 \pm$	0.60

Heating human serum albumin under the proper conditions forms particles that, when labeled with radioactive tracers, are very important in diagnostic procedures such as scintillation scanning of the lungs. In the course of determining the optimum conditions for preparing such labeled aggregates of high specific activity, it has been found that careful control of pH, salt content, rate of heating, and maximum temperature is necessary inasmuch as these factors have a large effect on the particle size formed.

IRON-52

In anticipation of resumption of operations of the newly rebuilt cyclotron, a series of chromium foils has been prepared by electrodeposition; with these the $\text{Cr}^{50}(\text{He}^{3,n})\text{Fe}^{52}$ reaction will be studied as a possible superior means of preparing Fe^{52} for medical application studies. Calculations indicate that the range of 60-MeV He^3 particles in chromium should be 0.05 in.

STRONTIUM-87m GENERATORS

Several years ago a simple milking system was developed whereby 2.8-hr Sr^{87m} is made available from a generator containing its 80-hr Y^{87} parent. Since 1963 we have supplied these generators at a constantly increasing rate until the demand reached the point in 1967 that private industry was willing to take over the production. However, before withdrawing from their distribution, we improved the generator in three ways:

(1) The size of the generator's ion-exchange column was reduced, permitting a higher concentration of product.

(2) Sodium bicarbonate solution (0.15 M) was found to be a satisfactory eluant; it is simpler to prepare than the previously used citrate solution

and more compatible with biological systems than NH_4HCO_3 , which had been briefly considered.

(3) Product contamination was reduced to $<10^{-4}\%$ Y^{87} at the time of milking.

P. RICHARDS, M. GREENE, J. BARANOSKY,
J. PASSARELLA

Analytical Chemistry Research

L. NEWMAN

MIXED LIGAND COMPLEXES

Nickel(II) Halides in Acetonitrile

The purpose of this investigation was to study the degree to which mixed halide complexes of nickel form in acetonitrile and to measure their formation constants. Salts of $[(\text{C}_2\text{H}_5)_4\text{N}]_2 \text{NiCl}_4$ and $[(\text{C}_2\text{H}_5)_4\text{N}]_2 \text{NiBr}_4$ were added to acetonitrile containing $[(\text{C}_4\text{H}_9)_4\text{N}] \text{ClO}_4$ as an inert electrode. The resultant solutions were studied spectrophotometrically. The existence of complexes of the form $[\text{NiBr}_{4-n}\text{Cl}_n]^{-2}$ was demonstrated. The constants for the formation of the three mixed species from the parent reactions were calculated. The values derived are shown in Table 2 along with the constants expected if there is purely statistical mixing of the ligands. In most systems of mixed ligand complexes, the mixed species are generally formed in greater than statistically expected amounts. Theoretical studies based on electrostatics have been advanced to explain why this is generally true. For a few systems, however, it has been observed that the mixed complexes are formed in less than statistical amounts or even not at all. It is seen that this system is one of the rare examples where less than statistical formation is observed. A completely adequate explanation of this behavior has not yet been developed, although some suggestions have been advanced.

T. GILBERT, L. NEWMAN

Platinum(IV) Halides

A spectrophotometric study of some of the equilibria involved in the aqueous iodide replacement of chloride in PtCl_6^{-2} and of bromide in PtBr_6^{-2} has been made. The reactions were studied by measuring the spectra of $\leq 10^{-4} M$ solutions of PtCl_6^{-2} in 1.0 M chloride, or of PtBr_6^{-2} in 1.0 M bromide, to which various small amounts of iodide had been added.

The PtCl_6^{-2} -I-solutions approached equilibrium quite slowly at $\approx 25^\circ$, and the spectra were

Table 3

Equilibrium Constants for the $\text{PtCl}_6^{-2}\text{-I}^-$ and $\text{PtBr}_6^{-2}\text{-I}^-$ Interchange Equilibria at $\approx 25^\circ$ ($\mu = 1.0 M$)

	$10^3 K_1$	$10^3 K_2$	K_1/K_2
$\text{PtCl}_6^{-2}\text{-I}^-$	10	5.5	2
$\text{PtBr}_6^{-2}\text{-I}^-$	4	1.2	3

examined at regular intervals over a period of several days until equilibrium was obtained. The equilibrium was maintained only for a relatively short time as decomposition subsequently occurred. The $\text{PtBr}_6^{-2}\text{-I}^-$ system was much easier to study, since equilibrium was attained within a few minutes and the solutions were stable for at least several hours.

A preliminary analysis of the data, making use of both graphical and computational methods and taking advantage of the existence of several isosbestic points, led to the values for K_1 and K_2 given in Table 3.

If the *cis* and *trans* di-iodo complexes are formed in amounts dependent only on statistical effects, then K_1/K_2 should be 2.4. K_1/K_{2t} and K_1/K_{2c} should be 12 and 3, respectively, where K_{2t} is the constant governing the formation of the *trans* complex and K_{2c} that for the formation of the *cis* complex.

The results in Table 3 show no evidence that the relative values of the constants are governed by anything other than statistical effects. Other studies on these systems had suggested, however, that the oxidation of PtX_4^{-2} by I_2 leads, under certain conditions, to *trans*- $\text{PtX}_4\text{I}_2^{-2}$, that this is in labile equilibrium with $\text{PtX}_5\text{I}^{-2}$, and that the reactions

and

are quite slow. It therefore seemed possible to study the equilibrium

in isolation from other equilibria. Such a study has been carried out on the chloride-iodide system. Spectral changes similar to those found previously are obtained, and a clear isosbestic point helps to

show under what conditions only one equilibrium is set up in the solutions. The equilibrium constant obtained from a preliminary analysis of the data is 2.7×10^3 and this is assigned tentatively to K_{2t} . If this is correct, then $K_{2c} \approx 2.8 \times 10^3$ and $K_1/K_{2t} \approx K_1/K_{2c} \approx 4$. Since K_1/K_{2t} should be 12 if the ratio were governed by statistical effects, a thermodynamic *trans*-effect does seem to exist, but the ratio K_1/K_{2c} is probably not distinguishably different from the value of 3 expected statistically.

A more thorough analysis of the data will be made in order to obtain K_1 and K_2 with greater precision, and further studies on the oxidation of PtX_4^{-2} with I_2 will be undertaken in an attempt to confirm the tentative value for K_{2t} obtained for the chloride-iodide system, and to obtain a value for the corresponding bromide-iodide equilibrium constant.

A. POË

MIXED β -DIKETONE COMPLEXES

Copper(II)

The divalent ion, copper, was selected for a systematic solvent extraction study to demonstrate the existence and stability in benzene of mixed β -diketone complexes with all possible combinations of furoyltrifluoroacetone (FTA), thenoyltrifluoroacetone (TTA), benzoyltrifluoroacetone (BTA), acetylacetone (AA), benzoylacetone (BA), and dibenzoylmethane (DBM).

The expression for the distribution of a divalent metal ion in the presence of two different chelating acids can be written as

$$D = \frac{[\text{MX}_2]_0 + [\text{MXY}]_0 + [\text{MY}_2]_0}{[\text{M}^{+2}]}, \quad (1)$$

where X^- and Y^- are the enolate ions of the two β -diketones. An equilibrium for the formation of each species can be written as

Substituting the form of Eq. (2) for each species into Eq. (1) and rearranging we obtain

$$D[\text{H}^+]^2[\text{HX}]_0^{-2} = K_X + K_{XY}R + K_YR^2 \quad (3)$$

where $R = [\text{HY}]_0/[\text{HX}]_0^{-1}$, K_X is the constant for the extraction of MX_2 , K_Y is that for MY_2 , and K_{XY} that for MXY .

Table 4
Summary of Constants^a

System X/Y	Log constants			
	K_X	K_{XY}	K_Y	K_m
TTA/FTA	-0.86	-0.5	-0.74	0.3
BTA/FTA	-1.20	-0.7	-0.72	0.3
BTA/TTA	-1.20	-0.8	-0.92	0.3
AA/BA	-4.18	-3.6	-3.70	0.3
DBM/AA	-3.74	-3.7	-4.14	0.2
DBM/BA	-3.74	-3.4	-3.70	0.3
AA/FTA	-3.70	-1.7	-0.70	0.5
BA/FTA	-3.56	-1.6	-0.68	0.5
DBM/FTA	-3.58	-1.7	-0.74	0.5
AA/TTA	-3.70	-1.9	-0.82	0.4
BA/TTA	-3.56	-1.7	-0.76	0.5
DBM/TTA	-3.70	-1.7	-0.82	0.6
AA/BTA	-3.82	-2.1	-1.22	0.4
BA/BTA	-3.64	-1.9	-1.16	0.5
DBM/BTA	-3.66	-2.0	-1.14	0.4

^aTotal chelate was maintained at 0.2 *M*. Aqueous phase was 2 *M* LiClO₄ and organic medium was benzene.

The equilibrium in the organic phase is therefore

The value of K_m is equal to $K_{XY}(K_XK_Y)^{-1/2}$.

Data were obtained by a titration technique where initially the weaker chelate, HX, is present. The distribution of the metal is measured by taking aliquots of both phases after increments of HY are added and equilibrated. The pH was monitored and maintained constant, and the volumes of both phases were kept equal. The data were plotted as $\log D + 2 \log [H^+] - 2 \log [HX]_0$ vs $\log R$. The constants were determined graphically by using the normalized curve technique of Sillen.

As can be seen from the results summarized in Table 4, the resolved values of the equilibrium constant for the extraction of the simple β -diketone complex are reasonably independent of the β -diketone with which it was paired. It can also be observed that $K_{XY} \geq K_Y$ when K_Y is only slightly greater than K_X , independent of whether the pair consisted of the strong or weak class. When a chelate from both classes is present, $K_Y \gg K_X$, then K_{XY} has a value intermediate between K_X and K_Y . Finally, when either two strong chelates or two weak chelates are present, the $\log K_m$ values are equal to the statistical value of 0.3. However, when

Table 5
Summary of Constants^a

System X/Y	Log of constant					
	K_X	K_{X_2Y}	K_{Y_2X}	K_Y	mK_{X_2Y}	mK_{Y_2X}
TTA/FTA	-2.6	-2.1	-1.8	-2.3	0.4	0.6
BTA/FTA	-3.8	-2.8	-2.3	-2.4	0.5	0.6
BTA/TTA	-3.8	-2.9	-2.5	-2.6	0.5	0.5
BA/AA	-6.6	-6.1	-6.0	-6.5	0.4	0.5
DBM/AA	-7.0	-6.3	-6.1	-6.5	0.5	0.6
DBM/BA	-7.0	-6.4	-6.1	-6.6	0.4	0.6
AA/FTA	-6.3	-4.1	-2.6	-2.5	0.9	1.2
BA/FTA	-6.4	-4.2	-2.6	-2.4	0.9	1.1
DBM/FTA	-6.9	-4.7	-2.8	-2.4	0.7	1.1
AA/TTA	-6.3	-4.2	-2.8	-2.8	0.9	1.2
BA/TTA	-6.5	-4.5	-2.9	-2.7	0.7	1.1
DBM/TTA	-6.9	-4.8	-3.0	-2.8	0.7	1.2
AA/BTA	-6.3	-4.6	-3.6	-4.0	0.9	1.2
BA/BTA	-6.5	-4.7	-3.6	-3.9	0.9	1.2
DBM/BTA	-7.0	-5.3	-4.0	-4.0	0.7	1.0

^aThe total chelate was maintained at 0.2 *M*. Aqueous phase was 2 *M* LiClO₄ and organic medium was benzene.

a weak and strong β -diketone are present, the stability of the mixed ligand complex appears to be somewhat enhanced. This correlation is qualitatively in keeping with the observation made by Marcus, Eliezer, and Zangen for a whole host of aqueous mixed ligand complexes; i.e., the greater the difference between the parent binary complexes, the stronger was the mixed complex.

L. NEWMAN, P. KLOTZ

Indium(III)

The existence of mixed β -diketone complexes with an element having an oxidation state of three was studied. In this case there can exist two mixed complexes in the organic phase, namely, MX_2Y and MY_2X , having formation constants K_{X_2Y} and K_{Y_2X} , respectively, defined in a way similar to that given by Eq. (2) of the preceding section. The equilibrium reactions in the organic phase are

with formation constants mK_{X_2Y} and mK_{Y_2X} , respectively. The results are summarized in Table 5. The β -diketones listed on the left are the weaker extractants in any given experiment. The equilibrium constants obtained for the simple extraction of the β -diketone complex are again independent

of the chelate with which they were paired. These empirically determined values agree quite closely between experiments.

When the chelate strengths are similar, as in the first six experiments, the equilibrium constants for K_{X_2Y} and K_{Y_2X} are for the most part stronger than the constants for the simple β -diketone extractions. When the chelate strengths are dissimilar, as in the remaining nine experiments, the value for K_{X_2Y} is intermediate between those of the parent chelates, but K_{Y_2X} is approximately equal to the constant for the stronger chelate. As was the case in the divalent metal study, there is a definite trend in the values for the mixed species resulting from the organic phase interaction of the two indium β -diketonates. When the β -diketones are of similar strength the values of mK_{X_2Y} and mK_{Y_2X} are approximately equal to the statistical value which in this system is 0.5 as opposed to 0.3 in the divalent system. When dissimilar chelates are used the stability of the mixed β -diketone complex is increased markedly.

L. NEWMAN, P. KLOTZ

MIXED-METAL COMPLEXES

With the use of both spectrophotometric and solvent extraction data, evidence has been obtained for the existence of a mixed-metal complex containing indium(III), chromium(III), and a hydroxy carboxylic acid. The characteristic that the organic acid must have is the malic acid structure

Consequently, such acids as malic, citric, isocitric, and tartaric were found to produce the mixed-metal complex. The elimination of any of the groupings or the interpositioning of another carbon group between the carboxylates or between the hydroxide was found to prevent formation of the complex. Consequently, such acids as glutaric, tricarballic, dicrotalic, α -hydroxyglutaric, or itamalic acids were found not to yield the complex.

Further studies will be performed to elucidate in greater detail the properties of mixed-metal complexes.

T. GILBERT, L. NEWMAN, P. KLOTZ

ELECTROCHEMISTRY OF TECHNETIUM

A Digital Data Acquisition System (DDAS) has been built for the study of electrochemical phe-

nomena. The DDAS samples a voltage transient at programmed intervals. The DDAS has been used in chronoamperometric studies of the electrochemistry of pertechnetate ion in basic media. The mechanism appears to involve a second-order disproportionation of Tc(VI) or Tc(V). There is also a marked effect of gelatin, a surfactant substance, on the initial reduction step. In the absence of gelatin the initial reaction is a two-electron process while in the presence of gelatin it is a one-electron process. This phenomenon has not yet been interpreted.

S. FELDBERG, G. KISSEL

DIGITAL SIMULATION OF HYDRODYNAMICS IN ELECTROCHEMISTRY

Two commonly used electrochemical techniques, polarography at the dropping mercury electrode and voltammetry at the rotating disc electrode, involve hydrodynamic phenomena. Both techniques have been successfully simulated and permit theoretical treatment of a wide variety of electrochemical mechanisms. Studies of the oxidation of substituted terphenylamines at a rotating platinum disc have been shown to involve a bimolecular coupling as an intermediate step. The rate constants have been evaluated from working curves calculated by digital simulation.

S. FELDBERG, R. ADAMS,* L. MARCOUX*

EDUCATIONAL FILM STRIP

Electrochemical diffusion-kinetic phenomena are complex and are at present a difficult challenge for the student attempting to grasp some of the basic concepts. It has, in fact, been observed that even those students capable of handling formidable mathematics often lose sight of the physical implications of the problem.

As a pedagogical aid computer-generated time-lapse photographs have been produced of the concentration profiles in electrolysis. The CRT photographs can be assembled as a film strip or they can be converted to 16 mm and assembled as a movie. Several strips will be produced depicting fundamental electrochemical techniques and processes, and their effectiveness as teaching aids will be evaluated.

S. FELDBERG, R. RODGERS**

*University of Kansas, Lawrence, Kansas.

**Summer student.

**EVALUATION OF CHEMICAL KINETICS
FOLLOWING ELECTRON TRANSFER
AT A TRANSPARENT ELECTRODE**

Certain glasses (e.g., tin oxide-coated glass) are surface conductors. By using a glass of this type as an electrode the products and intermediates of an electron transfer reaction can be studied directly using spectrophotocchemical techniques. A prerequisite, of course, is that the species of interest absorb photons at some wavelength. In order to

evaluate the kinetics of the oxidation of orthotolidine, digital simulation was used to predict the absorbance-time relationship for a quasi-reversible second-order mechanism:

Table 6
Shipments of Special Isotopes

Number									
1967									
Isotope	1965 ^a	1966 ^a	Jan/Feb	Mar/Apr	May/June	Jul/Aug	Sep/Oct	Nov/Dec	Total
Tc ^{99m} ^b	761	365	—	—	—	—	—	—	—
Mg ²⁸	154	97	6	8	10	3	5	8	40
I ¹³² ^b	73	55	7	7	6	—	—	—	20
Mo ⁹⁹	26	23	—	—	—	—	—	—	—
Sr ^{87m} ^b	19	53	26	15	—	—	—	—	41
Te ¹³²	12	7	4	3	3	—	—	—	10
I ¹³³	9	8	1	1	1	3	1	1	8
Y ⁹⁰ ^c	3	3	—	—	—	—	—	—	—
Y ⁹⁰ ^b	1	—	—	—	—	—	—	—	—
Ga ⁶⁸ ^b	1	—	—	—	—	—	—	—	—
Cu ⁶⁷	1	—	—	—	—	—	—	—	—
I ¹²³	1	—	—	—	—	—	—	—	—

Activity										
1967										
Isotope	1965 ^a	1966 ^a	Jan/Feb	Mar/Apr	May/June	Jul/Aug	Sep/Oct	Nov/Dec	Total	Unit of activity
Tc ^{99m} ^b	122,120	64,200	—	—	—	—	—	—	—	mCi
Mg ²⁸	23,400	16,500	900	1,100	1,150	400	350	800	4,700	μCi
I ¹³² ^b	780	560	90	70	60	—	—	—	220	mCi
Mo ⁹⁹	9,990	9,320	—	—	—	—	—	—	—	mCi
Sr ^{87m} ^b	25	163	80	45	—	—	—	—	123	mCi
Te ¹³²	88	80	60	40	40	—	—	—	140	mCi
I ¹³³	180	142	20	20	20	80	20	20	180	mCi
Y ⁹⁰ ^c	1,300	600	—	—	—	—	—	—	—	beads ^c
Y ⁹⁰ ^b	100	—	—	—	—	—	—	—	—	mCi
Ga ⁶⁸ ^b	30	—	—	—	—	—	—	—	—	mCi
Cu ⁶⁷	1	—	—	—	—	—	—	—	—	mCi
I ¹²³	0.5	—	—	—	—	—	—	—	—	mCi

^aCalendar years.

^bGenerators.

^cIndividual unirradiated beads.

where species A is the orthotolidine, and the absorbance of either species B or C is monitored. Preliminary experiments have indicated good agreement with theory. S. FELDBERG, T. KUWANA,* G. STROJEK*

EXPERIMENTAL AND THEORETICAL AUTOMATION

The Digital Data Acquisition System (DDAS) for acquiring electrochemical data over a wide dynamic range of time and signal amplitude has greatly increased the quantity and precision of our data. In order to properly analyze these large quantities of data, it was necessary to resort to computer (CDC 6600) analysis. The necessary programs have been written for converting the paper punch tape (put out by the DDAS) to magnetic tape, interpreting the magnetic tape, analyzing the data, and plotting the data in the appropriate mode.

The digital simulation programs used to generate the theoretical curves for various electrochemical techniques and mechanisms have been modified to produce the theoretical output in graphical form. Direct comparison can then be made between theoretical and experimental plots. S. FELDBERG, R. RODGERS

DEVELOPMENT

Diversified development work was undertaken in many fields of investigation. Oxygen was determined in alloys containing various combinations of Nb, Zr, Hf, Ta, Mo, W, and Ti by utilizing the inert gas fusion technique with gas chromatographic end determination. Spectrophotometric or atomic absorption procedures to determine 1 to 2% antimony in lead were developed. Development in the field of atmospheric diagnostics included a chemical process for extracting SO₂ from large volumes of air for quantitative analysis and determinations of S³²/S³⁴ isotopic ratios. Methods were developed for the quantitative determination of milligram amounts of In, Sn, Ag, and Cd individually dissolved in metallic sodium and for microgram quantities of Fe, Cr, and Ni. A method developed for analysis of carbon lamellar compounds of both potassium and cesium overcomes

*Department of Chemistry, Case-Western Reserve University, Cleveland, Ohio.

Table 7

Foreign Distribution of Special Isotopes^a

Destination	I ¹³³ (21 hr)	Mg ²⁸ (21 hr)	Sr ^{87m} ^b (2.8 hr)
Canada	1	9	6
England		1	
France		1	
Norway		1	

^aNumber of shipments of each isotope made in calendar year 1967; half-life of each isotope shown in parentheses.

^bGenerator.

problems arising from the pyrophoric nature of these compounds. Modifications of existing methods were made for analysis of alloys and individual metal hydrides.

Hot Laboratory Operations

P. RICHARDS

ISOTOPE PRODUCTION

As mentioned above, Brookhaven has for practical purposes withdrawn from the production of all short-lived radioisotopes, except for Mg²⁸ which will still be produced here on a reduced basis, and certain special isotopes that are produced for on-site experimentation and evaluation in connection with our program to develop medical applications of isotopes. Tables 6 and 7 illustrate graphically the extent of the reorientation of this work. It is interesting to note that after our withdrawal from Tc^{99m} generator production in 1966, the demand for our Sr^{87m} generators began to increase sharply until production of this isotope, too, was turned over to private industry in 1967.

A few shipments of Mo⁹⁹ were produced and distributed on an emergency basis to a former customer, when the ORNL supply failed temporarily. We have also been buying Mo⁹⁹ with which to prepare our own Tc^{99m} generators for on-site use; it has been found desirable to put the purchased material through our own purification process to reduce the volume, the NH₄⁺ concentration, and the I¹³¹ contamination.

Some of the items prepared for on-site study include Tc^{99m} as pertechnetate ion, labeled iron-ascorbic acid complex, labeled DTPA, labeled

Table 8
Summary of Liquid Waste Operations

“F” Waste Released to Sewer			
	Gal	Average activity level, Ci/ml	Total activity, mCi
Dec. 26, 1966, to Dec. 25, 1967	1,673,820	4.0×10^{-12}	25.1
Dec. 26, 1965, to Dec. 25, 1966	2,324,135	4.65×10^{-12}	40.8

Waste Concentrator Operations				Activity in mCi	
Waste to evaporator ^a		Concentrate ^a	Volume reduction	Feed	Distillate
1967 ^b	204,675	1,926	104 : 1	7,361	3.81
1966 ^b	271,125	3,369	80 : 1	8,030	0.434

“D” Waste Inventory				
	Gal start	Gal received	Gal to evaporator	Gal end
Dec. 26, 1966, to Dec. 25, 1967	86,195	183,495	204,675	65,015
Dec. 26, 1965, to Dec. 25, 1966	57,185	300,135	271,125	86,195

^aGallons.

^bNominal years (all other periods are exact years as shown).

sulfur colloid, labeled human serum albumin, and high specific activity macro-aggregated labeled albumin, all for various scintillation scanning studies, Sr^{87m} for bone studies, Kr⁷⁹ for brain circulation studies, and tritiated water.

P. RICHARDS, J. BARANOSKY,
G. WALKER, J. PASSARELLA

RADIOGRAPHY

Some 1631 radiographs were produced during the year, as opposed to the 2150 produced last year. Radiographic examination was made of the construction of new sodium loops, repairs to the HFBR heavy water cooling system, laminated superconductors, ceramic insulators, NaI(Tl) counting crystals, weld inspection of in-pile components of a crystal spectrometer, stainless steel-clad cobalt sources, several cryostats, and the chemonuclear loop.

J. AUSTIN, H. RUGE

LIQUID WASTE OPERATIONS

The inventory of radioactive liquid waste was 65,015 gal at the end of the year compared to 86,195

gal at the start. A total of 204,675 gal were processed by the waste concentrator during the year. Table 8 summarizes the liquid waste operations for the year. J. BARANOSKY, A. MACAULAY, W. AUSTIN, W. GRAY, G. WALKER, W. SCHMITZ, A. DENSIESKI

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Metallurgy and Materials Science Division

D.H. GURINSKY

This report describes all work sponsored by the Fuels and Materials Branch of the Division of Reactor Development of the US AEC and performed in the Nuclear Engineering Department of Brookhaven National Laboratory during the period January 1 to December 31, 1967.

Work sponsored by the Fuels and Materials Branch falls into three general areas: corrosion of fast reactor materials by liquid sodium, effects of irradiation on reactor materials, and properties of high-temperature refractory compounds.

Liquid Metal Center

During the year, preliminary results were obtained in all three major areas of the sodium corrosion program for fast reactors: materials testing, corrosion mechanisms, and chemistry of liquid Na solutions. This work is being performed as part of the AEC's Liquid Metal-Cooled Fast Breeder Reactor Program. The forced-circulation, boiling Cs, Nb-1% Zr loop remains in standby condition for future operation as manpower limitations permit.

MATERIALS TESTING PROGRAM

C. J. KLAMUT

The materials testing program is designed to evaluate the corrosion and mass transfer by liquid Na of potential containment and fuel cladding materials for use at 760° to 815°C.

Thermal convection loops are being used to evaluate the corrosion behavior of a broad spectrum of potential fuel cladding materials, and forced circulation loops are being used to study the corrosion behavior of selected materials under typical in-reactor conditions of Na velocity, surface-to-volume ratio, and heat flux.

A cobalt alloy development program is also under way to develop a nonembrittling cladding material suitable for operation at 815°C in the presence of Na and a fast flux.

Sodium Thermal Convection Loop Program

Corrosion of high-temperature materials in high-purity hot-trapped Na and in diffusion cold-trapped Na is being evaluated in a series of thermal convection loops. A schematic drawing of the thermal convection loop is given in Figure 1. About 40 test specimens, measuring $\frac{3}{8} \times \frac{1}{2} \times 0.013$ in., are suspended in a "rack," shown in Figure 2, over a temperature gradient of $\approx 660^\circ$ to 760°C in the hot leg of each loop. The specimens are metallographically polished on one side. They are removed at ≈ 1000 -hr intervals and weighed, and their surface composition is determined by x-ray fluorescence. Loop piping materials are type 316 stainless steel (SS), type 321 SS, and Haynes-25 alloy. The materials under test and their compositions are listed in Table 1.

The current status of the test program is shown in Table 2. The loop is constructed of $\frac{1}{2}$ -in. schedule 40 pipe with a 6-in.-long by $1\frac{1}{2}$ -in.-diam tank above the hot leg for increased Na inventory. The inside surface of the hot leg is ground and polished to a mirror finish to eliminate surface irregularities. The loop heaters consist of a double wrap of sheathed Nichrome wire along the hot leg of each loop and are capable of producing ≈ 4 kW. The cold leg of each loop is cooled by pulling air through holes in the sheet metal containments housing each loop. Na sample buckets and the corrosion test specimens are inserted and withdrawn from the loop through a removable 4-ft-long by $\frac{5}{8}$ -in.-diam pipe gas lock. Na samples are caught in two double-walled buckets of 1 and 3-g capacity which are attached to the bottom of the test rack.

A diffusion cold trap filled with Na_2O_2 is attached to the bottoms of the cold-trapped loops. The hot-trapped loops have Zr sheet attached to the bottom and top of the specimen rack. Each loop is filled with ≈ 1 lb of high-purity hot- and cold-trapped Na which is circulated for ≈ 1 wk under operating conditions. Two sampling buckets held in the loop's hot leg during the equilibration period are removed at this time for oxygen analy-

Figure 1. Schematic of Na thermal convection loop, showing gas lock.

Figure 2. Corrosion test section and sample bucket arrangement in thermal convection loops. Scale in inches.

Table 1

Corrosion Test Materials

Material	Composition
Iron-Base Alloys	
304 SS	Fe, 18% Cr, 8% Ni
304 SS(Ti)	Fe, 18% Cr, 8% Ni, 0.2% Ti
316 SS	Fe, 18% Cr, 12% Ni
321 SS	Fe, 18% Cr, 10% Ni
ORNL alloy	Fe, 15% Cr, 4% Al, 1% Y
Cobalt-Base Alloys	
Haynes-25	Co, 20% Cr, 10% Ni, 2% Fe, 15% W
Haynes-25	Co, 19% Cr, 18% Ni, 12% W
UMCO 51	Co, 28% Cr, 19% Fe, 2% Cb
S-1	Co, 20% Cr, 10% Ni, 7% Mo
Union Carbide 188	Co, 20% Cr, 15% Ni, 12% W
High-Nickel, Mixed-Base Alloys	
Multimet	20% Ni, 21% Cr, 20% Co, 32% Fe, 3% Mo, 2.5% W, 1% Cb + Ta, 0.1% N
Incoloy 800	32% Ni, 21% Cr, 45% Fe, 0.3% Cu
Refractory Base Alloys	
	V, 20% Ti
	V, 15% Ti, 7.5% Cr
	Mo
	Mo, 0.5% Ti, 0.1% Zr

sis. New buckets and the corrosion test specimens are then inserted into the loop for test. About every 1000 hr the specimens are removed from the loop and weighed and the oxygen content of the loop Na is determined. During the year the corrosion test specimen holder was redesigned to permit easier loading and discharge of specimens. The rack shown in Figure 2 is the holder now in use.

Results of Loop Tests. Some 23,000 hr of testing have been accumulated. The results of the loop tests to date are summarized below.

1. Maximum weight losses are $< 1 \text{ mg/cm}^2$ in a 1000-hr period and decrease with temperature.
2. Alloys containing the highest percent Ni (In-800 and Multimet) undergo the greatest weight loss.
3. Ni is leached from the surface of all the test specimens, with the greatest depletion occurring in the hottest regions.
4. Cr is leached at the higher temperatures only and is "apparently" deposited at lower temperature. Some specimens at lower temperatures show a gain in weight. Oxidation of the alloys, i.e., for-

Table 2
Status of Na Thermal Convection Loop Program

Loop No.	Time in hr	Loop material	Test specimens	Na environment
1-148	4635	321 SS	316 SS; S-1; IN-800	100°C diffusion cold trap
2-149	3872	"	316 SS; Haynes-25; Multimet	" " " "
3-150	3308	"	316 SS; S-1; IN-800	Zr hot trap
4-151	2125	"	Haynes-188; Haynes-25; UMCO-51; Multimet	" " "
5-152	2958*	"	Cu-plated 304 SS capsules pressurized with 942 psi He	140°C diffusion cold trap 510°C hot leg
6-153	Start-up	Haynes-25	Haynes-188; Haynes-25; S-1; UMCO-51	100°C diffusion cold trap
7-154	1085	316 SS	316 SS; S-1; IN-800; 304(Ti) SS	" " " "
8-155	To be filled	"	316 SS; S-1; IN-800; 304(Ti) SS	Zr hot trap
9-156	" " "	"	Haynes-188; Haynes-25; 316 SS; UMCO-51	" " "
10-157	" " "	"	Haynes-188; Haynes-25; UMCO-51; Multimet	100°C cold trap
11-158	" " "	"	304 SS(Ti); 316 SS; 304 SS; Fe, 15% Cr, 4% Al, 1% Y	" " "
12-159	In process	"	Mo; Mo, 0.5% Ti, 0.1% Zr; V, 20% Ti; V, 15% Ti, 7.5% Cr	" " "
13-160	" "	321 SS	Mo; Mo, 0.5%Ti, 0.1% Zr; V, 20% Ti; V, 15% Ti, 7.5% Cr	Zr hot trap
220	5000*	U, 20% Ti	None	" " "
*Test completed.			**Loops operate at 660° to 760°C, except as noted.	

mation of Cr₂O₃-rich scale, could explain the effects noted at low temperatures.

5. Based on weight loss data, Co-base alloys have equal or better corrosion resistance than type 316 SS.

Test results on the Cu-plated, He-pressurized type 304 SS capsules tested in a type 321 SS loop (140°C cold-trapped Na) at 510°C are being evaluated. This loop (a test to determine the effect of Cu in Na on the creep-rupture properties of 304 SS) was shut down after 2956 hr of operation when one of the capsules ruptured. None of the capsules had any Cu left on their surfaces. Metallographic examination of the burst specimen and portion of the loop is in progress. No Cu penetration has been detected in either the burst type 304 SS capsule specimen or in the 321 SS loop wall. Cu de-

posits were found just above the valve to the diffusion cold trap. Measurements of the diameters of the remaining capsules are in progress to determine the amount of creep.

A. FLEITMAN, J. BRANDON

Development of Cobalt-Base Alloys for 760°C Sodium-Cooled Fast Reactor Fuel Cladding

An appraisal of materials available for cladding Na-cooled fast reactor fuels operating at a maximum temperature of 760° to 815°C is shown in Table 3. No commercial tubing or sheet alloy meets all the prerequisites, but the most promising overall combination of properties was found in Co-base alloys. Commercial Co-base alloy sheet or tube, however, either lacks the desired creep-rupture

Table 3
Appraisal of Fuel Cladding Materials for High-Temperature Na-Cooled Fast Breeders

Material	Advantages	Disadvantages
Iron-base alloys	Excellent nuclear properties. Proven Na compatibility at 1200°F. Good compatibility with oxide fuels.	Low creep strength at high temperatures. Irradiation embrittlement found in SS.
Nickel-base alloys	Good nuclear properties. High strength properties.	Poor Na compatibility at high temperatures. Subject to irradiation embrittlement.
Cobalt-base alloys	Good strength properties. Na compatibility believed equal to or better than that of SS. Reasonable nuclear properties.	Activation to Co ⁶⁰ and possible mass transfer to heat exchanger. Information lacking on fuel compatibility or irradiation embrittlement. Some alloys embrittle at high temperatures.
Mo alloys	High creep strength. Excellent resistance to Na-bearing oxygen. Very high melting point ($\approx 2610^\circ\text{C}$). Commercial tubing alloys available.	Breeding ratio below those of Fe, Ni, Co, and V alloys; poor fabricability and weldability.
Refractory-base alloys (Nb, Ta, etc.)	High creep strength. High melting points. Commercial tubing alloys available.	High neutron cross section. Poor corrosion resistance in cold-trapped Na. Embrittled by O, N, or C.
V-base alloys	Good nuclear properties. Adequate strength.	Limited resistance to cold-trapped Na. No commercial alloys, but extensive alloy development under way.

Table 4
Experimental Cobalt-Base Alloys, 2nd Phase

Heat No.	C	S	Si	Mo	W	Ni	Fe	Mn	Cr	B	Ti
67-562	0.024	0.005	<0.01	5.03	5.23	7.14	3.15	0.24	20.77	<0.001	-
67-563	0.002	0.005	<0.01	5.13	5.47	9.92	3.10	0.04	20.57	<0.001	-
67-564	0.007	0.005	0.03	5.10	5.42	7.12	3.15	0.26	20.66	<0.001	2.16
67-565	0.007	0.004	0.01	4.55	5.00	9.92	3.15	0.01	20.71	<0.001	2.00
67-566	0.001	0.003	0.05	4.80	5.01	10.00	3.05	0.01	20.57	<0.001	3.05
67-567	0.043	0.004	<0.01	0.10	11.70	17.40	0.20	0.04	19.03	0.001	1.85
67-568	0.044	0.003	0.06	0.02	11.84	17.96	0.18	0.02	19.03	0.001	2.97
67-569	0.10	0.004	0.04	0.06	13.46	11.28	1.20	0.40	19.11	<0.001	-

ture strength or is susceptible to embrittlement by metallurgical changes and by fast-neutron irradiation. Thus a cooperative Co alloy development program was undertaken between the Haynes-Stellite Division of Union Carbide Corp. and Brookhaven National Laboratory. One of the primary objectives was to develop a Co alloy with creep-rupture properties at 1500°F that were equal to those of 304 SS at 1200°F.

Fifteen experimental alloys in the initial phase of the program were prepared and fabricated into sheet and plate. Details of the program are given

in Informal Report BNL 11530. The alloys with the best stress-rupture properties at 815°C were those containing titanium. On the basis of these tests eight additional alloys of the compositions shown in Table 4 were prepared and are being evaluated.

An evaluation of the data to date indicates the following:

1. Additions of 2 to 3 wt % Ti to Co alloys are effective age hardeners and stabilize the fcc phase.
2. Overaging can occur at 1550°F within 24 hr in some of these alloys. For long-time use, alloys

containing Ti would have optimum creep strength at temperatures below 1550°F.

3. For maximum response to age hardening, alloys containing Ti must be water-quenched. In this condition, they have 40 to 60% elongation and <20 R_c hardness.

A. FLEITMAN, J. CHOW,
R. HERCHENROEDER*

Forced Circulation Loop Program

Two forced circulation loops (FCL-1 and 2) constructed of stabilized SS have been completed. The first loop has been put into operation, and the second will be started up shortly. The corrosion resistance of potential fuel cladding materials for fast breeder reactors will be evaluated at high Na velocity in the loops. Figure 3 is a schematic diagram of these loops.

The unique feature of the loops is that heat is generated in the test section, which results in an inlet-to-outlet temperature rise of $\approx 50^\circ\text{C}$. The specimens will be removed periodically from the test section into a dry box and cleaned and their weight changes will be measured. The materials to be evaluated in the first test section of FCL-1 are shown in Table 5. The test section layout is shown in Figure 4. A number of preliminary runs have been completed in FCL-1 in which the loop components were tested. Na was circulated throughout the main circuit with both electromagnetic pumps. All auxiliary circuits were also opened sequentially. Performance of all components was satisfactory.

Several cold-trapping runs were made to reduce the oxygen concentration in the Na. With 3 gpm circulating at 270°C in the main circuit, cold-trapping was carried out at a flow of 0.2 gpm. Cold-trap temperatures ranged from $\approx 200^\circ\text{C}$ at the beginning to 140°C at the conclusion of the runs. During this period the oxygen meter was calibrated.

A test section mock-up containing surface thermocouples was inserted into FCL-1 in order to calibrate the outside tube wall temperatures with the corresponding specimen surface temperatures. The geometry of this section was the same as that of the corrosion specimen test section, except that six thermocouples were inserted into longitudinal slots in the test section. The couples were spaced around the diameter and along the length of the test section.

*Union Carbide Corp.

Table 5

FCL-1 - Run 1 Test Materials

Specimen No.	Material
1	Haynes-25
2	UMCO-51
3	Molybdenum
4	321 SS
5	Haynes-25
6	304 SS

NOTE: Each container (see Figure 4) holds 6 specimens, as listed above, except for specimens 9-1 to 9-6 and 10-1 to 10-6 which are all Haynes-25, in order to study the downstream effect on this material.

Runs were made at a number of test section temperatures and flow rates. Temperature, pressure drop, and flow rate data were accumulated for these runs. Wall and Na temperatures at the specimen surface agreed fairly well, except for a hot spot that was observed with both wall and Na thermocouples at a point ≈ 2 in. below the upper bus bar. The Na thermocouples indicated a 70°C rise and the wall thermocouples a 25°C rise above bulk Na temperature. At the time the hot spot was attributed to a possible blockage of the Na annulus by one of the thermocouple wires.

Following the temperature profile run, the FCL-1 test section was assembled and inserted into the loop. To prevent vibration of the test section at high power levels, the upper flanges were spring-loaded. The appearance of a hot spot ($\approx 700^\circ\text{C}$) in the same region in which one had been observed under high power conditions indicated that the test section was eccentric with the surrounding wall. This caused uneven Na flow in the annulus and overheating on the narrow side, as was confirmed by radiography of the test section. The loop was drained after only 24 hr of operation under these conditions. Two additional sets of pin spacers were added between specimen holders so that, in the heated region, centering pins were located every 7 in. along the test section length. The pins protruded 0.035 in. into the annular gap. The test section was reassembled (it was necessary to remove the tenth mandrel) after the specimens were reweighed and inserted into the loop. After start-up, an attempt was made to reach design conditions. No vibration or hot spot

Figure 3. Flow sheet of forced circulation Na corrosion loops.

problems were encountered at this time. However, in order to reach 760°C outlet temperature, the flow rate was reduced from 25 to 21.6 ft/sec and the minimum loop temperature was raised from 480° to 560°C. The loop was operated under the following average conditions for 1 wk, and then was shut down because of recurrence of the hot spot problem.

Max loop Na temperature	760°C
Test section ΔT	$\approx 50^\circ\text{C}$
Min loop Na temperature	560°C
Flow rate	5.5 gpm
Test section velocity, a_v	21.6 ft/sec
Oxygen level	5 to 10 ppm
Power input to test section	17.1 kW
Power input to preheater	20.3 kW

An apparently rapid shift in O₂ meter calibration during the period preceding the start of the test run has invalidated emf measurements from this unit until a new curve can be established. However, plugging runs and O₂ analysis of Na from a newly installed bypass sampler show that the O₂ level during the operating period was in

Figure 4. Test section of FCL-1 and 2, showing positions of specimens and bus bars.

the 5 to 10 ppm range. Two amalgamation results showed 6 and 7 ppm O_2 in the Na.

During the seventh day of operation a hot spot developed in the same region as before, and the loop was shut down. The test section was removed from the loop, the residual Na vacuum was distilled, and the specimens were weighed. Examination of the test section revealed that one of the guide pins in the region of the observed hot spot had apparently broken off. This may have resulted in eccentricity of the test section.

The results of the weighing of the specimens after the 1-wk run (run 1A) may be generally summarized as follows:

1. After 168 hr, weight losses were observed for all materials except Mo, which essentially did not change in weight.

2. For each of the corroding alloys progressively greater weight loss was observed for specimens with higher test section (increasing temperature) location. The change in weight vs temperature data was different for each alloy.

3. The corrosion rates of all the materials, except Mo, at $760^\circ C$ were in the 2 to 4 mils/yr range.

Because of the hot spot problem, a new test section was developed for use with the same specimens. The basic concept of this new section is to guide and center each mandrel with its six specimens within the loop tubing, but to allow freedom of movement between mandrels, so that each mandrel will follow the contours of any bend within the heated section. To this end the mandrels were drilled and slipped over a $\frac{1}{4}$ -in.-diam 321 SS rod. The fit is loose enough to allow freedom of motion between mandrels during insertion. Provision is made for tightening the mandrels and specimens after they are in place. With this flexibility, the height of each guide was increased from 0.035 to 0.045 in. Following each run the test section is loosened and removed.

Upon conclusion of a successful 2-wk run under the same operating conditions as those for run 1A, the Na was drained and the test section removed. The first two mandrels are shown in Figure 5, and the results of the weight-change measurements are shown in Figure 6. These data may be generally summarized as follows.

1. All materials, except Mo, continued to lose weight but at a lower rate than after 1 wk. Mo essentially did not change in weight.

2. For each of the corroding alloys greater weight losses were observed at higher temperatures.

Figure 5. Upstream end of test section from FCL-1 after completion of run 1B, showing specimens 1-1 through 1-6 and 2-1 through 2-6.

Figure 6. Corrosion rate data after completion of run 1B (2-wk data).

3. The corrosion rates for all the materials except Mo have apparently not reached a steady state.

Several minor modifications were made in the flexible test section design. The test section was then reassembled and inserted into the loop, and the loop prepared for start-up.

A. ROMANO, S. WACHTEL, W. TREMEL,
R. MITCHELL, F. ISELI, M. SCHUSTER

High Heat Flux Corrosion Loop

Preliminary design has been started for a High Heat Flux Corrosion Loop. The loop will be used to investigate the corrosion rates of potential cladding materials at temperatures as high as 760°C under conditions of high heat flux. Process conditions will be chosen to simulate, as nearly as possible, those of interest in a Na-cooled fast breeder reactor.

In the test section of the loop, tubular cladding specimens will be heated from one side with an intense [up to 1×10^6 Btu/hr-ft² (320 kW/cm²-sec)] heat source and cooled from the other side by high-velocity liquid Na.

Figure 7. Na solubility chamber.

Because there are no well-developed high-flux heaters, preliminary heater testing will be made in a small pump heater test loop, now under construction. In this test section designs will be tested at conditions to be achieved in the larger loop.

Two high-flux heating systems have been purchased for testing: (1) a 50-kW, 10 kHz motor-generator-type induction heater; and (2) an electron bombardment heater and power supply. The first of these units is widely used as a heating source (although never as a high-flux heater) and will supply heat through an induction coil to the test section. It differs from the radio-frequency (450-kHz) induction heater, which has previously been used as a high-flux heater, in that the depth of heat generation for the lower frequency unit is much greater and the voltage in the induction coil is an order of magnitude lower.

The electron bombardment heater, being built by the Eimac Division of Varian Associates, is essentially a vacuum diode; the filament and cathode are in the center of the tubular heater, and the anode is the sheath of the heater. This relatively new type of heater is in use at at least three installations. There are still a number of problems to be overcome in the use of this heater, especially the frequent occurrence of what appear to be arcs between cathode and anode. Construction of the heater test loop should be completed early in 1968.

A. ROMANO, S. WACHTEL,
J. BRANDON

SODIUM CORROSION MECHANISM PROGRAM

J. WEEKS

The purpose of this program is to determine experimentally the several thermodynamic and kinetic parameters that control the rate of corrosion of materials by liquid Na. Measurements to be made include the following: a reinvestigation of the solubilities of Fe, Cr, Ni, Co, V, Zr, and Ti in liquid Na and the effects of nonmetallic impurities (O, C, N, and H), both singly and in combination, on the measured solubilities; a determination of the kinetics of dissolution of these metals into Na, both as pure metals and as alloys, and the dependence of these kinetics upon such variables as nonmetallic impurities in the Na, temperature, temperature differential, and Na flow rate; and a study of the nature of any complex oxides that may form at the interfaces between steels and Na. Such oxides have been thought to have a major effect on the corrosion rate of the steels.

Preliminary results were obtained during the year on the solubilities of Cu, Fe, and Ni in Na, and the apparatus for studying the corrosion kinetics was nearly completed.

Solubility Studies

The apparatus designed to determine the solubilities of various metals in Na has been constructed, checked, and operated. A schematic is shown in Figure 7. Hot-trapped Na is vacuum-distilled through a Nb-1% Zr tube into the crucibles. The crucibles (Fe, Ni, and Cu) are leak-checked and hydrogen-fired before insertion into the solubility chamber.

The crucible and sampling cups, after being sealed into the solubility chamber, are given another hydrogen treatment at 600°C for 1 hr. The Mo sampling cups and the Mo-lined solubility chamber are then outgassed for ≈ 24 hr at a temperature exceeding the highest anticipated experimental temperature. The system is then pressurized with an ultrapure grade of helium that has been passed through a laboratory purification train.

Na vacuum-distilled at 500°C condenses in the Nb-1% Zr tube at $\approx 200^\circ\text{C}$ and drains into the crucible. The filled crucible and chamber are again pressurized, raised to the desired experimental temperature, and equilibrated for up to 24 hr. Twin Mo buckets are then lowered into

the melt, temperature-equilibrated, agitated to ensure their being filled, and raised. The temperature of the melt is then adjusted to another equilibration temperature, and the sampling procedures are repeated. Duplicate samples can be taken at each of seven temperatures. The sealed solubility chamber is then delivered to the analyst's dry box, where the duplicate samples are prepared for oxygen and metal analyses at each of the investigated temperatures. Preliminary experiments have established handling procedures and eliminated the difficulties of providing filled sampling cups (2 g Na). To date, >180 samples have been taken and sent for analysis.

Copper. The solubility of Cu in Na was measured at temperatures between 255° and 547°C . A Cu crucible made from zone-refined Cu sheet was loaded into the solubility apparatus. Na was directly transferred from the hot-trapped storage tank into the apparatus. After an equilibration period of at least 24 hr, duplicate samples were taken for analysis. This procedure was repeated at each of seven temperatures before the samples were unloaded in the analyst's dry box.

The results of the first run show considerable scatter at temperatures below 300°C and suggest that fine particulates were present in the Na cooled to these temperatures. In addition, the lower bucket occasionally contained ≈ 10 times as much Cu as the upper bucket. Consequently, a second run was made in which the same Cu crucible and Na were used; after an initial equilibration at 550°C , the apparatus was cooled to $\approx 250^\circ\text{C}$ for 24 hr, and all subsequent samples were taken after the melt temperature had been raised to the equilibration temperature. The results of the second run were more self-consistent than those of the first.

During the two complete runs, oxygen analyses of three samples did not exceed 15 ppm (amalgamation technique). The samples were analyzed for Cu by atomic absorption spectroscopy. The results for all samples are shown in Figure 8. The analytical reagent blank for these runs averaged $<1\ \mu\text{g Cu}$. Three results do not fit the other data in Figure 8, presumably because of the above-noted particulate Cu.

The results are compared with those of Humphreys at Los Alamos Scientific Laboratory and McKisson et al. at Atomics International in Figure 9. All three investigations are in good agreement

Figure 8. Solubility of Cu in Na: BNL data.

above 400°C, and the temperature dependence of the BNL results agrees with that of Humphreys.

Iron. Fe solubility measurements have been made at temperatures between 370° and 540°C. The Fe crucibles were irradiated in the Brookhaven Graphite Research Reactor for periods of up to 1 month. Two Fe standards were also included in each irradiation package. In each irradiation excellent Fe⁵⁹ counting agreement was obtained between standards. The results obtained with crucibles I and II are shown in Figures 10 and 11. Unirradiated Fe results obtained spectrographically are shown as filled circles in these figures.

No reasonable line can be drawn through the data at this point. The scatter in the results, however, suggests the presence of particulate Fe in the melt. Experiments are now under way to determine if particulates are indeed present and to resolve the discrepancy between the results of the radiochemical and spectrographic analyses.

Nickel. Ni solubility runs have been completed at the following temperatures: 340°, 367°, 390°, 420°, 446°, 474°, 485°, and 495°C. Results

Figure 9. Summary of available data on the Cu-Na liquidus.

for the first four temperatures will not be reported because of high sample blanks in the colorimetric analysis. The results obtained at the four higher temperatures are shown in Figure 12, except for data, which tended to be high, from samples weighing <1 gram. The data scatter appreciably, so that a reasonable curve cannot be drawn at this time. The average solubilities range from 0.7 ppm at 446°C to 2.8 ppm at 495°C.

R. SINGER,
W. BECKER, J. SAULS

Corrosion Kinetics

The corrosion rate of stainless steels in Na with low levels of oxygen impurity^{1,2} is determined by the corrosion rate of a ferritic iron layer that forms on the surface of the alloy, after a period of corrosion during which Ni and Cr are preferentially leached. The mechanism for the leaching of Ni appears to result from a simple solution mechanism, whereas for Cr the mechanisms involved are not clear. Cr initially forms an oxidized surface layer implying an oxide or complex oxide formation.¹ The corrosion rate of Fe is dependent on oxygen concentration,³ which precludes a simple

¹A.W. THORLEY AND C. TYZACK, *IAEA Conf. on Liquid Metals*, Paper SM-85/18, IAEA, Vienna, 1966.

²R.W. LOCKHART, GEAP-4438, 1964.

³*Liquid Metals Handbook, Sodium NaK Supplement*, J.W. Mausteller and G.G. Voorhees, Editors, p. 94, TID-5277, 1955.

Figure 10. Data on the solubility of Fe in Na, crucible I.

Figure 11. Data on the solubility of Fe in Na, crucible II.

solubility process; but as the corrosion behavior of pure Fe has not been determined, it is usually considered to be the same as that of steels with the ferritic iron surface layer. The possibility that alloying elements reduce the activity of the iron at the corroding interface has not been considered, but it may explain some of the effects observed during the corrosion of steels.

The corrosion behavior of the pure metals that are constituents of stainless steels will be investigated to obtain a clearer understanding of the part played by each element in the corrosion of stainless and other steels. The corrosion rates of these metals will be determined as a function of temperature, time, oxygen concentration in the Na, and velocity. The apparatus will consist of a Mo container with a cold trap within a stainless steel vessel. It will be possible to add or remove samples at the operating temperature and thereby prevent complication of the measurements by heating and cooling cycles which would influence results taken over short periods of time. Samples will be corroded under almost static (thermal convection) conditions, and the effects of velocity will be investigated under otherwise

Figure 12. Solubility of Ni in Na.

identical conditions by rotating cylinders of different diameters attached to the same spindle. This method will not be complicated by "downstream" effects or influenced by the variations in cold-leg residence times that occur with loops.

Components have been designed and machined, and the apparatus is being assembled. A major difficulty arose when the brittle heat-affected zone of the Mo cracked during welding of the inner container as a result of the thermal stresses induced. The design of the Mo container was altered and the difficulty overcome. The container will be heat-treated to relieve mechanical stresses and reduce the possibility of its cracking during operation.

A Na distillation unit is being constructed to supply high-purity Na for this apparatus, so that the corrosion of metals can take place without complicating side effects from impurities.

H. ISAACS, W. BECKER

Figure 13. Apparatus for Na-O reaction studies.

SODIUM CHEMISTRY PROGRAM

L. NEWMAN

The over-all objective of this phase of the program is to gain an understanding of the chemistry of Na coolant systems and of the chemical aspects of corrosion processes in Na. The program includes studies of reactions and interactions between Na and its impurities and container materials, studies aimed at elucidating the nature of impurities in Na, and development of sampling methods and analytical techniques which are specific for certain impurities or forms of impurities in Na.

Sodium Corrosion and Impurity Chemistry

These studies are directed at obtaining thermodynamic and kinetic information on Na impurity-metal reactions, including equilibrium constants, free energies and heats of formation, and reaction kinetics. In addition, the nature of impurities as well as interactions between impurities and reaction products, in Na or on surfaces in contact with it, will also be studied to provide insight into reaction mechanisms and aid in interpretation and/or development of chemical analysis methods.

B. MINUSHKIN

Studies on Sodium-Oxygen Chemistry. The corrosion rates of many metals in Na are dependent on the concentration of oxygen. In addition there is evidence that carbon transfer is also influenced by oxygen. To obtain a more detailed knowledge of these corrosion mechanisms, studies were initiated of the reactions and interactions between oxygen and other impurities (such as metals, carbon, hydrogen, and other gases) in Na.

A solid electrolyte galvanic cell is the basic tool in these studies. Under proper conditions the emf developed by this cell will be determined by the oxygen potential (or activity) of the Na. The basic experimental technique will be to introduce non-metal and metal reactants into the Na and measure the emf developed by the oxygen meter. Any reactions involving oxygen must result in changes in the partial molar free energy of oxygen in Na, which will be reflected as a change in cell emf. Analysis of the rate of change of emf will provide information on kinetics of the reaction, and equilibrium values will provide information on thermodynamic properties of the Na solutions.

The equipment needed for these measurements has been completed and preliminary tests are in progress. The essential features of the apparatus

are shown in Figure 13. Na is contained in a beaker supported on a pedestal within the 4½-in.-diam SS vessel. A liquid-metal oxygen meter is positioned at the top of the tank so that the electrode is immersed ≈ 1 in. below the Na surface. The vessel is equipped with a gas lock through which metallic or nonmetallic reactants or impurities can be introduced into the Na and Na samples can be removed. The vessel is also equipped with a sealed, magnetically coupled stirrer. The ½-in.-diam Na fill/drain line can be retracted and used to withdraw cover gas samples during the test. An electric furnace (not shown) surrounds the SS tank. Temperature is measured by two thermocouples, one contacting the bottom of the Na beaker and the second in a sheathed well immersed in the Na. In preliminary tests at 316°C, these two thermocouples agree within 1°C. The proportioning temperature controller used with the apparatus held the temperature constant within $\pm 1^\circ\text{C}$. Two setups of this design and a third, similar apparatus have been constructed.

Shakedown tests on the apparatus have been completed. Present studies include a method of calibrating the oxygen meter electrode *in situ*, a method of removing (gettering) oxygen from Na at relatively low temperatures, and methods for making quantitative additions of materials to the Na.

At least one method for calibrating oxygen electrodes and gettering oxygen from Na appears to be satisfactory; it consists of successively gettering oxygen and adding known amounts of oxygen to the Na. The observed changes in meter voltage provide a calibration of the electrode. This method avoids the uncertainties of sampling and chemical analysis.

The gettering material had to be one that would use only a small area of its surface to remove oxygen from Na rapidly at a relatively low temperature. Ca, Li, Zr, Zr/Ti alloy, and U were tested. The soluble getters Ca and Li were very effective in reducing oxygen activity at temperatures as low as 300°C. However, they cannot be removed from the Na and may interfere with subsequent reactions. The oxidation rates of Zr and Zr-50 wt % Ti alloy added as foil and powder were too slow at 400°C.

U foil was found to be useful in the calibration procedure. About 40 cm² of 11-mil electropolished U foil is immersed in ≈ 800 g Na while the voltage developed by the oxygen meter is measured. Dur-

ing oxidation in Na at 400°C an adherent oxide film is found on the U. Its thickness is a linear function of exposure time. The weight change of the U is thus proportional to the oxygen gettered from the Na, and by comparing it with the corresponding change in electrode voltage it is possible to calibrate the meter. Quantitative additions of oxygen (as Na₂O) at 400°C were also made in an independent determination of the meter calibration. The two calibrations agreed reasonably well.

B. MINUSHKIN, H. ISAACS, R. DOERING,
W. BECKER, V. WILLIAMS

Studies on Sodium-Carbon Chemistry. Liquid Na-gas reactions will be conducted to obtain basic information on Na-nonmetal systems. The Na-C system is of particular interest, and the use of gaseous carbon compounds will enable controlled addition of carbon (in various forms) to excess Na at the ppm level. Absorption processes will be studied by following pressure changes with time. The nature of both the gaseous and the solid reaction products will be investigated. From the kinetics of the reaction and the composition of the products it is hoped to distinguish the active forms of carbon in solution from those that are particulate, and perhaps to deduce the carbon solubility. The apparatus has been constructed and is now being calibrated.

M. HOBDELL

Electromigration Studies. Studies of electromigration of oxygen and other impurities were undertaken to elucidate the nature of these dissolved impurities in liquid Na. Although electromigration of oxygen to the anode in molten Na has been reported in the Russian literature [B.A. Nevzorov, AEC-tr-5412 (1962)], U.S. attempts [*Development of Techniques for Measurement of Impurities in Sodium*, MSAR 67-18 (Feb. 7, 1967)] to reproduce this effect have thus far been unsuccessful.

Attempts made here have been inconclusive because of convective or bulk mixing of the Na during or after the test. Recent work has been directed toward developing an apparatus that would eliminate the possibility for mixing. The current version is shown in Figure 14; preliminary tests with Hg have been successful. The apparatus consists of a vertical 1-mm-i.d. quartz capillary tube, the lower end of which dips into Na contained in a 600-ml SS beaker. The upper end of the capillary is enlarged to a 12-mm-diam section above which is an upper capillary section containing the sealed electrical lead. Four capillary tubes are installed through seals in the beaker. After gas above

Figure 14. Electromigration apparatus.

the Na in the beaker is evacuated, the ends of the capillaries are immersed below the Na surface and the beaker is pressurized to fill the lower capillary and 12-mm section with ≈ 2 g Na. The Na in the beaker is the other electrode. Upon termination of electrolysis, the Na is rapidly frozen in place, and the 12-mm portion in the tubing is analyzed for oxygen.

In a typical test run two of the capillaries are electrolyzed, the third is used to sample the Na in the beaker before the test, and the fourth to sample the Na after the test. Tests will be conducted using current densities up to 1300 A/cm^2 and temperatures from 120° to 250°C .

C. AUERBACH,
B. MINUSHKIN

Sodium Chemistry Loop. The Na chemistry loop will be used to provide a controlled, well-characterized source of Na samples for analytical development and other experimental uses, to evaluate Na sampling and impurity monitoring methods, and to extend Na corrosion and impurity chemistry studies from bench-scale apparatus to a pumped Na system. Figure 15 is a schematic

flow diagram of the loop, which is expected to be in operation by January 1968.

B. MINUSHKIN,
A. ROMANO, A. KOKINELIS

Radiation Effects on the Electrochemical Oxygen Meter. A program has recently been initiated to evaluate the effects of radiation from primary system Na on the operation of electrochemical oxygen meters. During normal operation, the primary source of radiation will be Na^{24} , which will build up to a saturated specific activity of 0.1 to 0.2 Ci/g. Thus the meter in a reactor circuit will operate in the presence of 1.37- and 2.75-MeV γ 's and with 1.39-MeV β 's at the electrode surface. Estimates are being made of the maximum and minimum γ and β dose rates to the meter electrode. Tests will be performed within these calculated limits, using β and γ sources to simulate the energy levels and dose rates.

B. MINUSHKIN

Analytical Development

The purpose of this work is to develop standard sampling techniques and rapid, reliable analytical methods for determining trace impurities in Na and container materials. The work includes development of sampling techniques for use in the corrosion and chemistry programs, development of an isotopic dilution technique as a direct method for determining oxygen in Na, further development and comparison of amalgamation and vacuum distillation techniques, and development of methods and capabilities for determining C, N, H, and metallic elements in Na and container materials. In addition, analytical services are provided for the corrosion and Na chemistry programs.

Determination of Oxygen in Sodium. A number of experiments were carried out which were designed to afford a better insight into the size and cause of the blank associated with the amalgamation method for determining oxygen in Na and to compare the amalgamation and vacuum distillation techniques. In these experiments, manifolds consisting of five legs of $\frac{1}{2}$ -in.-o.d. $\times$ 12-in.-long SS tube were filled under vacuum with sodium which had been added at $\approx 130^\circ\text{C}$ and filtered through a $5\text{-}\mu$ sintered SS filter. In addition, a manifold with two legs was filled; one leg was allowed to cool slowly while the second was immediately quenched in liquid nitrogen. Samples of $\approx \frac{1}{2}$ to >2 g were cut from each leg and analyzed for oxygen content. In most cases the SS tube was carried along in the procedure, while in some cases the Na was extruded prior to analysis.

Figure 15. Schematic flow diagram of Na chemistry loop.

A blank of 5 ± 2 μg oxygen was consistently obtained for the amalgamation method in glass extraction vessels. This blank is routinely obtained for and applied to all samples analyzed in this program. To determine the blank, samples were divided into two or more portions varying in weight from $\approx \frac{1}{2}$ to 2 g. The total micrograms of oxygen for each portion were plotted versus weight, and the resulting straight line was extrapolated to zero weight to obtain the blank correction. The average value of 5 ± 2 μg oxygen is based on >20 independent determinations; typical results are shown in Figure 16.

A series of tests was conducted to determine which of the following possibilities is the cause of

this blank: (1) interaction with the glass extraction vessels, (2) contamination from the glove box atmosphere, (3) contamination from the SS tube carried along in the procedure, and (4) contamination introduced by the Hg.

To test the possibility that the blank is caused by (4), three adjacent samples of about the same weight were cut from one leg of a manifold and analyzed at the same time. Hg in amounts of 30, 60, and 90 ml, respectively, was used for the samples in the first extraction. The results are shown in Table 6. A factor of 3 variation in the initial quantity of Hg used produced no significant change in the total micrograms of oxygen or in the apparent blank.

Figure 16. Amalgamation method blank.

Samples analyzed by the amalgamation or vacuum distillation method consistently yield results ≈ 3 ppm higher when the SS tube is carried along in the extraction vessel (nonextruded) than when the sample is extruded from the SS tube before amalgamation. This difference, although small, was observed in nine comparisons, both for samples cooled slowly and for samples quenched after filling to minimize segregation of oxygen on cooling. These results suggested that SS sample tubes contribute a small error proportional to sample size (or surface area of SS). However, this cannot be the cause of the constant $5\text{-}\mu\text{g}$ blank.

It thus appears that the $5\text{-}\mu\text{g}$ blank is caused by the glass amalgamation vessels. The blank was found to be independent of the particular amalgamation vessel and of the age of the vessel. To prove this assumption a number of "piggyback" experiments were performed in which a secondary amalgamation vessel (the piggyback) was carried through the usual amalgamation procedure. The source of Na and Hg, however, was a "primary" amalgamation vessel in which amalgamation and washing had been carried out as usual. Oxygen concentrations of $5\text{ }\mu\text{g}$ were consistently found, which indicates that each glass vessel indeed con-

Table 6
Effect of Quantity of Mercury on Amalgamation
Method Blank

Sample	Initial quantity Hg used, ml	Total quantity Hg, ml	Sample weight, g	Total O ₂ , μg	O ₂ ,* ppm
M3 L5-4	30	150	1.21	11.6	6
M3 L5-5	60	180	1.07	11.2	7
M3 L5-6	90	210	1.09	9.8	5

* $4\text{-}\mu\text{g}$ blank correction applied.

tributes the same blank (see Table 7). These experiments also suggest that the $5\text{-}\mu\text{g}$ blank is obtained even in the absence of the heating associated with the initial amalgamation.

The size of the blank is directly related to the surface area of glass exposed to the amalgam. In additional experiments involving increasing amounts of glass surface, in the form of glass beads, an increase in the size of the blank was obtained, as shown in Table 8. Samples M3 L5-1, 2, and 3, to each of which 700 glass beads were added, yielded a blank of about $15\text{-}\mu\text{g}$ oxygen. Piggyback samples M3 L4, analyzed with 20 to 700 glass beads added, yielded blank values of 5.6 to $14\text{ }\mu\text{g}$ oxygen. Thus these two independent methods of determining the blank yield equivalent results.

A series of analyses was performed in a preliminary comparison of the amalgamation and vacuum distillation methods. The results (Table 9) indicate that at the 10-ppm level both methods yield comparable values. In addition, the results to date indicate a zero blank for the vacuum distillation technique.

The feasibility of using a Na ion electrode rather than atomic absorption for determining the Na in the Na_2O residues was explored. Although the sensitivity was satisfactory, the undue drifting of the measuring apparatus and the time-consuming procedure preclude convenient adaptation of this technique.

T. PRACH

Oxygen Analysis by Isotope Dilution Conversion of Oxygen in Sodium to Carbon Monoxide. The underlying principle of this method is to convert the oxygen species present in Na to CO by reaction with excess graphite. To obviate quantitative collection of the small amount of CO involved, a known amount of O^{18} is added to the sample; mass

Table 7

Effect of Amalgamation Vessel on Apparent Glass Blank

Sample	Amalgamation vessel No.	Sample weight, g	Piggy back O ₂ , μ g
M3 L1	9	0.928	6
M3 L2	6	1.30	5
M3 L2	13	1.74	5
M3 L2	2	0.83	5
M3 L3	13	0.80	4

Table 8

Effect of Glass Surface Area on Oxygen Blank

Sample	Sample weight, g Na	No. of 3-mm-diam beads added	Total O ₂ , μ g
M3 L5-1	0.812	700	18
M3 L5-2	1.48	700	22
M3 L5-3	2.40	700	25
M3 L4 piggy back	1.05	20	5.6
M3 L4 piggy back	1.02	100	6.0
M3 L4 piggy back	1.12	350	12
M3 L4 piggy back	1.04	700	14

Table 9

Comparison of Amalgamation and Vacuum Distillation Methods

Vacuum distillation		Amalgamation	
Sample weight, g	O ₂ , ppm	Sample weight, g	O ₂ , ppm
1.30	9	0.617	7
0.577	9	1.28	6
1.02	6	1.72	7
1.92	8	1.02	7
0.992	9	0.926	7
1.06	9	0.928	9

spectrometric measurement of the CO¹⁶/CO¹⁸ ratio in the evolved gas yields the oxygen content in the original sample. The method involves the following steps: (1) quantitative addition of a known amount of O¹⁸ to the Na sample; (2) vacuum distillation of the Na; (3) conversion of the oxygen present to CO based on the over-all reaction typified by $\text{Na}_2\text{O} + \text{C} = \text{CO} + 2\text{Na}$ [$\Delta G^0 = 118,050 - 90.0 T$ cal, G.N. KUZNEVNIKOV, *Zh. Prikl. Khim.* **38**, 479 (1965)]; and (4) mass spectrometric measurement of the resultant CO¹⁸/CO¹⁶ ratio. The critical step is (3), because the unfavorable thermodynamics

Figure 17. Apparatus for isotope dilution analysis for oxygen.

require rapid removal of the resultant Na vapor from the equilibrium.

The work is carried out in a Mo crucible (1/2-in. i.d., 1/16-in. wall thickness) mounted at adjustable distances from a water-cooled SS cold finger and heated by induction. A thermocouple is mounted in the bottom of the crucible, and the whole assembly is enclosed in a quartz jacket by O-ring seals. The apparatus is shown in Figure 17. Graphite powder, outgassed at 2000°C, is the source of carbon. Since use of both a 3-Mc and a 450-kc induction furnace resulted in production of an excited state of CO and almost complete loss of the gas, step (3) is carried out with use of a 10-kc motor-generator unit.

The reaction involved in step (3) has been studied by using pure dry Na_2O , which is believed to be the major oxygenated species in Na. CO is evolved slowly at 790°C and a useful rate of evolution is attained at 850°C . Good yields of CO were obtained, although difficulties in weighing the small quantities ($<400\text{ }\mu\text{g}$) of Na_2O involved precluded a quantitative evaluation.

It had been established in previous experiments that step (3) is not feasible in the presence of the bulk Na distillate because of the tendency of CO and Na to recombine. Consequently the distillation step (2) is performed separately; the crucible is then transferred, in the dry box, to another out-gassed jacket-cold finger assembly. Step (3) is now carried out by heating under vacuum to 720° to 730°C ; the stopcock is closed and the temperature raised rapidly to near 900°C . Evolution of CO is allowed to continue for 5 min.

Several experiments were performed in which Na samples were distilled in the presence of 0.2 g graphite. Blanks, in the absence of Na, yielded negligible amounts of CO. In these experiments the temperature in step (2) was allowed to go as high as 750° to 760°C (no significant CO release takes place at these temperatures). The decision to proceed to such high temperatures was made during the studies of the Na_2O -C reaction, when it was noted that Na began to distill at $<600^\circ\text{C}$, i.e., about 200° lower than the CO evolution temperature. The preliminary conclusion was that lamellar Na-graphite compounds are formed, as had been observed under somewhat similar conditions [W.C. SLEPPY, *Inorg. Chem.* 5, 2021 (1966)], and the high terminal temperature was chosen to insure complete decomposition of these compounds. Unfortunately this technique led to substantial losses of graphite (and, presumably, oxygen) from the crucible; attempts to minimize them were uniformly unsuccessful. Distillation is now done in the absence of graphite, and graphite is added during the transfer procedure, prior to step (3).

Distillations in the absence of graphite are terminated at 400°C ; it was observed that the oxygen-containing species will oxidize Mo if the temperature is allowed to go much higher ($<500^\circ\text{C}$ in the case of NaOH, just above 600°C in that of Na_2O). On the other hand, if the resulting Mo oxide(s) were quantitatively reduced to CO by graphite at a convenient temperature, there would be advantages in allowing the Mo oxidation to run to completion by distillation at about 700°C ,

because CO evolution in step (3) would then take place without formation of Na. Indications are that CO is indeed produced from Mo oxide(s) near 900°C , and this matter is under investigation. A blank was carried out by using pure Na (5 ppm oxygen by amalgamation), a terminal distillation temperature of 400°C , and the reduction procedure described above. The result corresponded to a yield of CO of about 50%.

Ag_2O^{18} is used as a source of O^{18} in step (1), the isotope dilution. Most of the exploratory work to date has been done by using regular Ag_2O to determine conditions for quantitative reaction between Ag_2O and Na. Encouraging results have been obtained by allowing the two substances in the evacuated crucible to be in contact for about 10 min at a temperature between 150° and 180°C . The yield of CO was about 30% (Ag_2O equivalent to $50\text{ }\mu\text{g}$ oxygen added to 1 g pure Na). Efforts are under way to provide better contact between Ag_2O and Na.

C. AUERBACH, T. PRACH,
R. SIEGEL

Analysis of Sodium for Trace Metallic Impurities.

Because of the number of impurities to be determined at very low levels, a spectrographic method of analysis was deemed most suitable. Precipitation of Na as NaCl with HCl and retention of the impurities in solution served to preconcentrate the impurities. Completeness of precipitation by gassing with HCl was verified, and tracers were used to determine the recovery of Fe, Ni, Cr, Co, and Mn; in addition, the lower limit of detection was established for each element. By using the dc arc technique, sensitivities of 0.1 ppm were easily obtained. The present procedure involves transfer of the sample from its container to a quartz tube, dissolution in methanol, and neutralization with HCl gas. Alternatively, distillation of Na from the dry sample is used in special cases.

To provide lower blanks, all Na work is conducted in a Fiberglas hood with a Lucite door. All stands and clamps are made of Lucite or Teflon, and a hot plate with a Corning Pyroceram top is placed in the hood only when needed.

Since it is apparent that the more important impurities are rarely below 1 ppm, the less sensitive but more precise atomic absorption method of determination is being explored for Fe, Cr, and Ni and has been used successfully for Cu. Further, modification of a conventional colorimetric procedure for Ni was satisfactory at the 1-ppm level. Currently under investigation for simultaneous

multielement analysis at the 1-ppm detectability level is an APDC-MIBK extraction followed by analysis by ac spark emission spectroscopy with use of a rotating disc. Preliminary experiments using Ni^{65} and Fe^{59} tracers have given encouraging results. J. FORREST, R. WILSON, D. LEAHY

Iron-59 Determination. A radioactive tracer technique is being utilized for the determination of Fe solubility in Na. The samples submitted had been contacted under varying conditions with pure (99.999%) irradiated Fe crucibles. The original intention was to count the samples and reference standards under standardized geometry, but γ spectrometry has shown that this approach is not feasible.

The major radioactive impurities in runs 1 and 2, which were contacted with Fe crucible No. 1, were Ta^{182} and Ag^{110} . Small amounts of Cr^{51} and Mn^{54} , the latter resulting from the (n,p) reaction on Fe^{59} , were also observed. Conventional chemical separation procedures were developed to separate the Fe from these impurities. As a result, a pure Fe^{59} fraction was obtained and counted.

γ Spectrometry of Na samples from runs 3 and 4, which were contacted with Fe crucible No. 2, showed the presence of Sb^{124} (major radioactive isotope) and small amounts of Cr^{51} and Mn^{54} . Fe was separated chemically by using the above procedures, and a carrier precipitation method was developed to remove small amounts of Sb^{124} . The

Fe^{59} fraction was subsequently analyzed by γ spectrometry. As little as $0.06 \mu\text{g}$ Fe per sample could be determined in this manner. M. KINSLEY

General. Service analyses for the materials and corrosion mechanisms program constituted the major activity during the year. Some effort was devoted to reactivating the apparatus for determining carbon in Na by the low-temperature oxidation method and setting up equipment for the determination of hydrogen in Na by a vacuum reflux technique described by Meacham and Hill (*The Determination of Hydrogen in Sodium Metal*, APDA-183, June 1966). Other efforts included colorimetric determination of boron in various fuel-cladding test alloys, and development of an analytical method for potassium-graphite compounds, which consists of combustion analysis for C and atomic absorption spectroscopy analysis for K.

T. PRACH, D. LEAHY, S. TASSINARI

Radiation Effects

Work in radiation effects during 1967 included studies of the effects on mechanical properties of stainless steels and cobalt-base alloys, the effects of work at cryogenic temperatures on the behavior of stainless steels under irradiation, and the effects of irradiation on the mechanical properties and microstructure of pure Fe.

Table 10

Tensile Properties of Cobalt-Base Alloys
(All specimens solution-treated at 1175°C ; strain rate, 0.002 in./min; irradiation temperature, $\approx 100^\circ\text{C}$.)

Alloy	Exposure, nvt ($E > 0.82 \text{ MeV}$)	Test temperature, $^\circ\text{C}$	Yield strength	Tensile strength	Total elongation, %
Haynes-25	0	25	67,000	152,000	55
Haynes-25	1.3×10^{20}	25	139,000	142,000	15
Haynes-25	0	800	35,900	41,500	10.5
Haynes-25	1.3×10^{20}	800	39,200	41,100	2.3
Multimet	0	25*	71,000	121,000	43
Multimet	1.3×10^{20}	25	116,000	138,000	31
Multimet	0	800	23,600	32,900	55
Multimet	1.3×10^{20}	800	30,000	31,300	6.7
S-1	1.3×10^{20}	25	114,000	118,000	4
S-1	1.3×10^{20}	800	23,600	23,600	1.5
Ht586**	1.3×10^{20}	25	136,000	141,000	44
Ht586**	1.3×10^{20}	800	23,600	31,000	4

*Tested at 0.02 in./min.

**Experimental alloy: 19% Cr, 12% W, 18% Ni, 1% Zr, 2% Fe, balance Co.

EFFECT OF IRRADIATION ON FUEL CLADDING MATERIALS

J. CHOW, R. JONES

Two studies have been in progress on the effect of irradiation on fuel cladding materials for use in the LMFBR. One study involves advanced cladding materials in cases in which the cladding temperature can get up to 760° to 815°C. The other study is concerned with the effect of microstructure on the elevated temperature ductility of irradiated stainless steels.

Cobalt-Base Alloys – Advanced Fuel Cladding

In the work on Co-base alloys for fuel cladding, the effect of irradiation on the tensile properties of such alloys is being investigated. The following alloys (see Table 1 for their compositions) are being studied: Haynes-25, S-1, UMC0 51, Multimet, Union Carbide Alloy 188, and several experimental alloys that are not embrittled by thermal aging. Pre- and post-irradiation tensile tests of all the alloys are being made at room temperature and at 800°C. The specimens were irradiated at about 100°C in an in-core facility of the HFBR to an exposure of 1.3×10^{20} nvt ($E > 0.82$ MeV).

The results to date are shown in Table 10. All the alloys tested indicate that Co-base alloys are embrittled at 800°C after irradiation in a manner similar to that for austenitic stainless steels and Ni-base alloys. The Haynes-25 and S-1 alloys also show an appreciable loss in ductility after irradiation when tested at 25°C. The Multimet and Ht586 alloys show an appreciable increase in strength at 25°C, but only a slight decrease in ductility. However, the elevated temperature strengths at 800°C are appreciably lower than those of Haynes-25.

The Co-base alloys are susceptible to aging embrittlement without irradiation by the formation of Laves and sigma phases and other intermetallic compounds. A slight adjustment in the balance of the alloying elements could cause a considerable change in the ductility of these alloys. The test data on Ht586, especially at room temperature, indicate that the ductility after irradiation is sensitive to variations in composition.

Metallographic examination is being done on the irradiated materials to study the changes in microstructure and their influence on the fracturing and mechanical behavior of the specimens.

Effect of Microstructure on the Elevated Temperature Ductility of Irradiated Stainless Steels

The nature of the high-temperature embrittlement of irradiated austenitic stainless steels indicates that the loss in ductility is sensitive to the microstructure of the materials. Studies elsewhere⁴⁻⁶ have shown that refining the grain size, cold-working, aging treatment, and addition of Ti to alter the precipitation are helpful in minimizing the embrittlement. All the methods studied have limitations on the extent of change possible in the grain structure and the distribution of carbides in an annealed stainless steel.

In the present study, the transformation of the metastable austenite to martensite is used to break up the prior annealed structure and to distribute uniformly a fine dispersion of carbides. The treatment consists of deforming the steel at 77°K (liquid nitrogen temperature) to 18 to 20% and reheating in the temperature range 650° to 815°C. Deforming type 304 SS at 77°K to 18% elongation will transform about 50% of the austenite to martensite. The martensite needles are very fine and homogeneously distributed throughout the austenite grains. Because of differences in carbon solubility between the austenite and martensite, the martensite formed is supersaturated with carbon. Tempering of the martensite causes a fine precipitation of carbides similar to that which occurs during tempering of quenched carbon steels. Increasing the reheating temperature to above 550°C causes the martensite to revert to austenite. The sequence of low-temperature deformation and reheating must be repeated to obliterate the original annealed grain structure. A treatment consisting of deforming 18% elongation at 77°K, annealing for 16 hr at 1300°F, deforming again to 18% at 77°K, and reannealing for 16 hr at 700° to 815°C has been selected for irradiation effect studies. This treatment produces in type 304 SS a material with a grain diameter of 0.003 to 0.005 mm (ASTM 11) and a fine, uniform distribution of carbides.

⁴W.R. MARTIN AND J.R. WEIR, Influence of grain size on the irradiation embrittlement of stainless steel at elevated temperatures, *J. Nucl. Mater.* 18, 108-18 (1966).

⁵P.C.L. PFEIL AND D.R. HARRIES, in *Symp. Flow and Fracture Behavior of Metals and Alloys in Nuclear Environments*, Chicago, 1964, pp. 202-21, ASTM Spec. Tech. Publ. 380, 1964.

⁶W.R. MARTIN AND J.R. WEIR, *Solutions to the Problem of High-Temperature Irradiation Embrittlement*, ORNL-TM-1544, June 1966.

Table 11

Tensile Properties of Unirradiated Type 304 SS
(strain rate, 2%/min)

Condition*	0.2 Yield strength, psi	Ultimate strength, psi	Total elongation, %
25°C Test			
Annealed	34,900	88,500	78
A + 650°C	90,400	129,500	37
A + 700°C	66,300	104,500	53
A + 760°C	37,400	98,000	60
A + 815°C	31,800	97,500	74
B + 650°C	94,300	132,500	31.5
B + 700°C	40,600	99,000	61
750°C Test			
Annealed	14,200	22,500	52
A + 650°C	29,600	30,600	40
A + 700°C	18,500	35,600	67
A + 760°C	16,200	23,600	73
A + 815°C	15,300	23,700	80
B + 760°C	15,800	21,300	87
B + 815°C	15,400	20,500	85

*Treatments: A, deformed 18% at 77°K plus annealing for 16 hr at indicated temperature; B, deformed 18% at 77°K, annealed 16 hr at 700°C, deformed again 18% at 77°K plus annealing for 16 hr at indicated temperature.

The tensile properties of unirradiated type 304 SS in the annealed condition and after various temperature-deformation and reheating pretreatments are presented in Table 11. The low-temperature deformation treatment increases the elevated temperature ductility if the final reheating temperature is 700°C or higher. Note that the double-strain and annealing pretreatment and annealing at 760° and 815°C produce material with 85 to 87% total elongation when tested at 750°C.

Specimens of type 304 SS given the double-strain and annealing pretreatments have been irradiated at $\approx 100^\circ\text{C}$ in an in-core facility in the HFBR to an exposure of 1.3×10^{20} nvt ($E > 0.82$ MeV) and tested at 25°, 650°, and 750°C. The results are presented in Table 12. The strengths after irradiation are generally lower than those for the pretreated specimens, but the total elongation at 650° and 750°C is significantly higher. For instance, at 750°C the annealed material shows a total ductility of 13%, but the pretreated specimens (reheated to 760°C) elongated 28%. However, the pretreated

Table 12

Tensile Properties of Irradiated Type 304 SS^a

Condition	0.2% Yield strength, psi	Tensile strength, psi	Total elongation, %
25°C Test			
Annealed ^b	81,500	105,000	58
B + 760°C	95,500	108,000	45
650°C Test			
Annealed	19,200	29,800	7.5
Annealed	24,800	31,700	14
B + 760°C	17,800	29,200	21.5
B + 815°C	21,600	24,800	15
750°C Test			
Annealed ^b	16,300	21,700	18
Annealed	15,800	18,100	13
B + 700°C	10,800	14,500	20.5
B + 760°C	12,300	14,200	28

^aAll specimens irradiated to 1.3×10^{20} nvt ($E > 1$ MeV); irradiation temperature, $\approx 100^\circ\text{C}$.

^bStrain rate, 0.020 cm/cm-min; strain rate for all other tests, 0.002 cm/cm-min.

^cB treatment: Deformed 18% at 77°K, annealed 16 hr at 700°C, deformed again 18% at 77°K plus annealing for 16 hr at indicated temperature.

specimens actually show a large loss in ductility because the unirradiated specimens under the same conditions had a total elongation of 87%. Metallographic examinations of these specimens are now being made to compare the mode of fracture.

These preliminary results are encouraging and it is planned to extend the study to include types 316 and 301 SS.

THE EFFECT OF FAST-NEUTRON IRRADIATION ON THE DEFORMATION OF IRON AND STEEL

S. MCRICKARD, R. JONES, A. CAMMARANO

Rate-Controlling Deformation Mechanism

The activation parameters for deformation in both as-received and irradiated Fe have been determined with use of a stress relaxation technique. During a tensile test, the stress was allowed to relax immediately after the yield point had been reached, and the time behavior of the tensile stress, σ , was

Figure 18. Effective stress of Ferrovac Fe as a function of temperature.

Figure 19. Dependence of the activation volume of Ferrovac Fe on the effective stress.

studied. The relaxation rate, S , was then determined from the slope of the $\Delta\sigma$ vs $\log t$ plot. From the analysis of Feltham [*Phil. Mag.* 6, 847 (1961)] the activation volume V^* for the controlling deformation mechanism can be obtained from $V^* = 2.3 kT/pS$, in which p is a constant (usually 0.5).

The applied stress, τ_a , has two components: τ^* , the effective stress at the rate-controlling barrier, and τ_i , the athermal long-range internal stress. τ_i was determined from high-temperature tests in which the yield stress is athermal and from the

residual stress after stress relaxation at room temperature. τ^* in Ferrovac Fe is independent of fast-neutron ($E > 1$ MeV) irradiation, as shown in Figure 18, and the variation of the activation volume with τ^* is also unaffected, as shown in Figure 19. The deformation mechanism at low strains is thus unaffected by irradiation.

The deformation mechanism of an Fe-0.014 wt % N alloy, however, was affected by irradiation. The deformation mechanism in this alloy below room temperature is different from that in unirradiated Ferrovac Fe; after irradiation, the deformation appears to become the same as in the Ferrovac Fe, as indicated by the thermal variation of τ^* and the plot of V^* vs τ^* shown in Figures 20 and 21. The major effect of fast-neutron irradiation in Ferrovac Fe is thus an increase in τ_i , and the deformation below room temperature must be controlled by some form of Peierls barrier to dislocation motion.

Defect Saturation and Radiation Sensitivity in Iron and Steel

Although saturation of radiation damage in metals has been theoretically proposed, it has not been observed in reactor steels. Work done here has shown that mobile carbon must play an essential role in radiation embrittlement, and that either the absence of sufficient carbon in solution or an irradiation temperature at which carbon is immobile prevents the onset of radiation embrittlement.

The yield stress data for Ferrovac Fe irradiated from 10^{15} to 10^{20} nvt ($E > 1$ MeV) at 50° to 100°C show good agreement with the saturation expression of Makin and Minter,⁷ as shown in Figure 22. Following the method of Diehl and of Nichols,⁸ the depleted zone size at saturation was calculated to be 4.4×10^{-19} cc. This corresponds to a spherical capture zone diameter of 95 Å and an actual zone diameter of ≈ 50 Å. The derived saturation fluence for the Ferrovac Fe is about 1.5×10^{19} nvt, which agrees with the experimental data. These results also match quite well the electron microscope observations of Eyre⁹ and Bryner,¹⁰ who first observed spots after 10^{19} nvt in Fe and loops after 10^{20} nvt or after annealing Fe ir-

⁷M.J. MAKIN AND F.J. MINTER, *Acta Met.* 8, 691 (1960).

⁸J. DIEHL, in *Radiation Damage in Solids*, Vol. 1, p. 129, IAEA, Vienna, 1962; F.A. NICHOLS, WAPD-T-1865, Oct. 1965.

⁹B.L. EYRE, *Phil. Mag.* 7, 2107 (1962).

¹⁰J.S. BRYNER, *Acta Met.* 14, 323 (1966).

Figure 20. Effective stress of Fe-N as a function of temperature.

Figure 21. Dependence of the activation volume of Fe-N on the effective stress.

radiated to 10^{19} nvt. Since these loops appear in Fe that has partially recovered the yield strength increase, they play no role in radiation hardening.

By investigating Ferrovac Fe containing varying amounts of carbon, low fluence deviations of the square-root dependence of the yield stress were shown to be related to the amount of carbon in solution. The amount of "available" carbon and the related microstructure are believed to control the mode of saturation and the saturation fluence. From the binding energies of possible carbon traps, the carbon locked in Fe_3C is considered unavailable for interaction with the depleted zones.

The yield stress data of quenched and tempered A212b and modified HY80 steels have been analyzed with use of this model. The results are shown

Figure 22. Yield stress data plotted against saturation expression, $\Delta\sigma = A(1 - e^{-B\phi t})^{1/2}$.

Table 13

Estimated Saturation Fluences for Iron and Steels

Material	Capture diam, Å	Actual diam (est.), Å	Saturation fluence ($E > 1$ MeV)
Ferrovac Fe	94	50	1.3×10^{19} nvt
Fe-0.1 C	66	33	4×10^{19}
A212b	61	30	5×10^{19}
HY80	41	20	1.6×10^{20}

in Table 13 along with the Fe data. They suggest that the Ferrovac Fe is the most sensitive to neutron irradiation and HY80 is the least.

Defect Analysis

A more detailed analysis is needed of the defect-producing changes in the mechanical properties of Fe and steel than that described in the preceding section. Studies are being conducted to identify the components and establish the kinetics of the dissociation of the defects.

Previous work established that C or N was necessary for enhanced radiation hardening and embrittlement of Fe; neither irradiations conducted at temperatures at which these interstitials are unable to move, nor post-irradiation annealing produce such damage. One or more components of the defect produced apparently migrate to different sinks if not immediately joined with C or N.

On the other hand, dynamic strain aging due to C and N is not observed after fast-neutron irradiation. Instead, cyclic serrations appear in the elevated temperature stress-strain curve after every 6 to 7% strain. In addition, the normal Snoek internal friction peaks due to C and N are not observed after irradiation. However, after a short anneal at 250°C a broad damping peak appears at 230°C. Both the appearance of this peak and the return of the Snoek peaks with annealing time and temperature are being studied.

The kinetics of loss of radiation embrittlement in Fe were studied. The time required for complete recovery of normal properties was plotted against the reciprocal of the annealing temperature; the slope of this plot yielded an activation energy of ≈ 0.4 eV. An electrical resistivity study of annealing kinetics in Ferrovac Fe irradiated to 2×10^{18} nvt at 70°C has given an activation energy of 0.5 eV. In both studies of recovery, however, the temperature of defect motion was $\approx 250^\circ\text{C}$, and the activation energies are thus anomalously low. Apparently more than one process is occurring simultaneously. Electrical resistivity studies of hydrogen-purified Fe are being run to eliminate this problem. Further, irradiations at 77° K will be run when the new low-temperature irradiation facility is inserted into the BGRR.

THE DEFORMATION OF NEUTRON-IRRADIATED IRON

P. SOO, R. JONES, J. HARE

Although neutron irradiation does not markedly alter the deformation parameters in bcc metals, small but significant changes do occur. Most experimenters agree that irradiation increases the yield stress for slip, possibly in an athermal manner. If differences in the homogeneity of slip do cause a change in the flow stress because of a strain rate effect, then the activation volumes and activation energies for slip would also be affected.

In the present program an attempt has been made to reduce the amount of inhomogeneous deformation in neutron-irradiated polycrystals of Ferrovac E iron. The experiments involve the irradiation of specimens that have been prestrained in tension to 9% elongation and irradiated at $\approx 90^\circ\text{C}$ to 1.3×10^{20} nvt ($E > 0.82$ MeV) in the HFBR. This procedure was designed to decrease substantially any strain rate effects that might otherwise have occurred.

The standard tensile specimen used in this study had a gage length of 1.125 in., a cross-sectional diameter of 0.120 in., and recrystallized grain size of 1.22×10^{-3} in. The interstitial impurity contents were 30 ppm C, 55 ppm O, and 5 ppm N.

Figure 23 shows the flow stresses for the unirradiated control samples. To produce a comparable dislocation substructure throughout the temperature range, all specimens were prestrained at room temperature prior to flow stress determination. A typical deformation sequence for a test temperature T is as follows. The specimen is deformed at T and a strain rate of 0.02 in./min just sufficiently to allow the lower yield stress to be determined; it is then prestrained at room temperature to a total elongation of 4½%; it is additionally strained ½% at T ; and the relaxation stress is followed. This sequence is repeated for 5% increments of strain.

In this work the shear stress τ has been taken to be $\sigma/2$, where σ is the average longitudinal stress. Below 300° K the flow stresses of the control specimens increased with strain in an approximately athermal manner. At temperatures $> 300^\circ\text{K}$, a deviation from this behavior was observed and the flow stresses began to increase with increasing temperature.

Activation volumes for slip were calculated from the stress relaxation tests with use of the theory de-

Figure 23. The effect of room-temperature prestrain and neutron irradiation (1.3×10^{20} nvt, $E > 0.82$ MeV) on the flow stress of Ferrovac E iron polycrystals.

Figure 24. The effect of room-temperature prestrain on the stress relaxation of Ferrovac E iron polycrystals at 223°K.

Figure 25. Activation volumes for slip in unirradiated Ferrovac E iron polycrystals as a function of strain and temperature.

veloped by Feltham (*op. cit.*) and Sargent [*Acta Met.* 13, 663 (1965)]. A typical set of relaxation data is given in Figure 24. The calculated activation volumes, given in Figure 25, are seen to be only slightly dependent on strain, except at 301°K. When they are replotted as a function of the temperature-dependent component of stress τ^* , the points all lie close to a single curve, as shown in Figure 26. τ^* was taken to be $\tau_T - \tau_{300}$, where τ_T is

Figure 26. Activation volumes for slip in unirradiated and irradiated Ferrovac E iron as a function of thermal (temperature-dependent component of) stress.

Figure 27. Activation energies for slip in unirradiated and irradiated Ferrovac E iron as a function of temperature.

the average stress during relaxation and τ_{300} is the stress at 300°K.

Activation energies for slip have also been calculated. Values of $d\tau/dT$ were obtained from the gradients of the curves in Figure 23. Although some scatter in the points is evident, especially at the higher temperatures, the results in Figure 27 define a single curve.

A typical effect of a neutron-irradiated dose of 1.3×10^{20} nvt on the flow stress of the prestrained material is shown in Figure 28. Although the prestraining treatment was not completely successful

Figure 28. A schematic representation of the effect of neutron irradiation on the flow behavior of prestrained Ferrovac E iron polycrystals.

in producing continuously uniform deformation throughout the gage length, there was an increase in observed ductility compared with that obtained on undeformed specimens irradiated to similar doses [S.B. MCRICKARD AND J.G.Y. CHOW, *Acta Met.* 14, 1195 (1966)].

Stress relaxation tests were conducted on the irradiated specimens at $\approx 10\%$ total elongation (point P in Figure 28), from which activation volumes and activation energies for slip were determined. The results are compared with those for the control samples in Figures 26 and 27. Both the activation volumes and activation energies have been decreased by irradiation; the activation energies were markedly affected at temperatures in excess of 150°K .

According to Fleischer [*J. Appl. Phys.* 33, 3504 (1962)], τ^* varies with the temperature as shown in the equation

$$(\tau^*)^{1/2} = A + BT^{1/2},$$

in which A and B are constants. The present results are also in excellent agreement with this relationship, as shown in Figure 29. The athermal component of stress has been taken to be equal to the flow stress at 327°K .

As has been shown above, neutron doses $> 2 \times 10^{19}$ nvt cause saturation of the yield stress increase in Ferrovac E iron. Thus the present irradiated material may contain small defect loops which would give rise to tetragonal distortions. The calculated activation volumes indicate that these defects are small and very closely packed.

It remains to be explained why previous work on the deformation of bcc materials irradiated in

Figure 29. The temperature dependence of the thermal-dependent component of stress for slip in neutron-irradiated Ferrovac E iron polycrystals.

the annealed state indicated that the basic rate-controlling glide mechanism was unaltered. It seems likely that, at strains in excess of the Luders strain (where most activation parameters were measured), many of the irradiation defects had already been swept out by the moving dislocations. The activation parameters subsequently measured were therefore representative of crystals having a denuded defect distribution, and the values would not be expected to differ appreciably from those in the unirradiated state.

ELECTRON-MICROSCOPIC STUDY OF THE EFFECT OF FAST-NEUTRON IRRADIATION ON THE MECHANICAL PROPERTIES OF IRON

J. BRYNER

Irradiation Effects on Electron-Transmission Substructures in Iron Strained at 77°K

Tensile tests of annealed Ferrovac E iron have shown that Fe irradiated to 2×10^{18} nvt or higher exhibit an abrupt ductile-to-brittle transition on cooling below 125°K , while unirradiated Fe retains ductility down to 4°K . The ductile-to-brittle transition in the irradiated Fe is characterized by an abrupt increase in the yield stress and an abrupt decrease in the fracture stress. The present

investigation was undertaken to determine whether the substructures resulting from strain at a temperature below that of the ductile-to-brittle transition might offer an explanation for the radiation embrittlement.

Experimental Methods. Circular disk specimens ≈ 0.020 in. thick were prepared from $\frac{3}{16}$ -in.-diam bars of annealed Ferrovac E, of which some were unirradiated and some had been irradiated at 60°C with fast ($E > 1$ MeV) neutrons to 2×10^{18} nvt. The disks were ground and polished to produce flat parallel faces.

Some of the disks were compressed under liquid nitrogen between polished tungsten carbide blocks; hardened steel guard washers were used around each specimen to limit the reduction in thickness to 0.5% to 40%. These disks were then ground from both sides to a thickness of ≈ 0.013 in. and electrolytically thinned to produce electron-transparent foil on the central plane. Other disks were electrolytically polished to remove surface strains and deformed by simple bending under liquid nitrogen to produce surface stresses slightly exceeding the known yield stresses. Residual deflections were measured to determine the amount of plastic strain at the surface.

The surfaces strained in tension were examined by optical microscopy. The tensile surfaces were then polished flat and the compressive sides were ground away. The resulting 0.10-in.-thick disks were electrolytically thinned to produce electron-transparent foils, on a plane midway between the neutral plane and the tensile surface, which were then examined by electron-transmission microscopy.

Results. Optical examination of the tensile surfaces of the bend specimens disclosed that in both irradiated and unirradiated specimens the plastic strain was limited to a narrow band approximately equal in width to the specimen thickness. The bands contained linear strain markings which were revealed by oblique illumination to be surface ledges; these were generally aligned at angles $< 45^\circ$ from the bending axis but otherwise showed no consistent pattern. Within individual grains, additional shallower strain markings were observed which were sometimes straight and parallel and sometimes wavy and intersecting. The markings on irradiated and unirradiated specimens were quite similar, in contrast to the findings reported by other investigators.

Surface cracks were found on all irradiated specimens strained plastically to $\approx 0.5\%$ surface elonga-

tion with the deformed bands. No cracks were found in unirradiated specimens after higher strains, which indicated that the irradiated specimens were indeed embrittled. All the surface cracks detected were > 1 grain diameter in length, so that the site of crack initiation could not be pinpointed. Many were discontinuous, which suggested that they were initiated at a point beneath the surface. Long cracks were transgranular along most of their length but always contained intercrystalline segments.

Figure 30*a* shows an as-bent area on an irradiated specimen containing typical strain markings, distorted grains, and a discontinuous crack. Figure 30*b* shows the same area after light wet-lapping to flatten the surface plus a light etch to show grain boundaries. The crack lies partially within one grain parallel to the boundary. After interruption by a thin web of metal, it runs along the boundary between the first grain and a second grain; then after interruption by a heavily deformed portion of the first grain, the crack runs partially into a third grain. Although the metal at the ends of the crack is heavily deformed, the metal along the sides of the crack shows no deformation, which indicates failure by cleavage. Figure 30*c* shows the same area after electropolishing to remove ≈ 0.0002 in. from the surface plus a light etch to reveal grain and twin boundaries. Strain markings due to deformation by slip are eliminated.

Comparison of Figures 30*a* and *c* shows that a continuous ledge crossing several grains may be due to twinning in some grains and to slip in others. It is apparent that the first and third grains adjacent to the crack in Figure 30*a* have a segment of common boundary beneath the surface which is parallel to the transgranular crack in the third grain. Extension of the crack in Figure 30*c* suggests that the crack was initiated on this common subsurface boundary segment and then propagated transgranularly in one direction and mostly intergranularly in the opposite direction. A small grain boundary crack in the upper right corner of Figure 30*c* is further evidence that cracking was initiated at subsurface grain boundaries. This crack was apparently initiated at a position where Figure 30*a* shows that ledges due to slip in one of the adjacent grains terminate on the boundary.

Electron-transmission examination of the specimens deformed slightly in tension at 77°K revealed the presence of twins and narrow bands or lines of

Figure 30. Optical micrograph of tensile surface of Ferrovac E iron specimen irradiated to 2×10^{18} nvt and bent to 0.5% surface elongation at 77°K. Nital etch, 860 $\times$. (a) Surface as bent, showing straight and wavy ledges and a short interrupted crack; (b) same area after mechanical polishing to remove ledges and etch to show relation of crack to grain structure; (c) same area after electrolytic polishing and etch to show grain and twin structure (note additional grain-boundary microcrack at upper right).

concentrated dislocations which probably corresponded to the surface ledges due to twinning and slip. Instances of transition from twinning to slip across a grain boundary were observed. High concentration of dislocations occurred where twins impinged on grain boundaries, which indicated high local strains and initiation of deformation by slip in one grain by twinning in a contiguous grain. Some cases of high concentrations of dislocations within the grain boundary suggested slip along the grain boundary. Additional dislocations distributed

randomly throughout the grains probably corresponded to the case of surface grains that were distorted but showed no strain markings. In regions of higher strain, networks of relatively straight dislocations were formed within the grains.

Attempts to examine the metal adjacent to cracks proved difficult, but in a few instances visual examination of a very narrow region was possible. In these cases the metal on each side of a transgranular crack and a grain boundary crack contained very few dislocations, which suggested brittle failure, but the metal within webs that interrupted cracks contained very high concentrations of dislocations, which indicated heavy distortion and appreciable ductility in the webs.

Electron-transmission structures observed in specimens deformed in compression at 77°K to 0.5% reduction in thickness were identical to those in the specimens deformed slightly in tension except that the amount of deformation varied less

Figure 31. Typical electron-transmission substructures in unirradiated Ferrovac E strained 0.5% in tension by bending at 77°K, showing twins, dislocation structures, and "internal dislocation sources."

Figure 32. Typical electron-transmission substructures in Ferrovac E irradiated to 2×10^{18} nvt and compressed 0.5% at 77°K, showing twins and dislocation structures, but no "internal dislocation sources."

Figure 33. Typical electron-transmission substructures in unirradiated Ferrovac E compressed 5.0% at 77° K, showing high concentrations of dislocations at grain and twin boundaries, dislocation networks within grains, and "internal dislocation sources."

Figure 34. Typical electron-transmission substructures in Ferrovac E irradiated to 2×10^{18} nvt and compressed 5.0% at 77° K, showing high concentrations of dislocations at grain and twin boundaries, dislocation networks within grains, but no "internal dislocation sources."

from one area to another in the compression specimens. Typical electron-transmission structures observed in unirradiated and 2×10^{18} nvt-irradiated specimens strained slightly at 77°K are shown in Figures 31 and 32, respectively. The only apparent effect of irradiation on the structures is that the unirradiated grain matrices contain small patches of concentrated dislocations, while the irradiated grain matrices do not. This same difference was previously observed in specimens strained at ambient temperature. The small patches of concentrated dislocations were considered to be evidence for internal dislocation sources in the unirradiated Fe.

Electron-transmission examination of specimens compressed to higher strain levels at 77°K showed that with increasing strain the concentration of dislocations increased but the concentration of twins did not increase appreciably. This observation indicates that twinning at 77°K is inhibited by prior deformation by slip. Within the grains, the dislocations formed increasingly dense networks of relatively straight, uniformly distributed dislocations which appeared to lie parallel to $\langle 111 \rangle$ directions or to projections of $\langle 111 \rangle$ directions on the foil plane, which suggests that these dislocations are primarily screws. At grain boundaries, at twin boundaries, and along bands or lines of dislocations, extremely dense tangles of dislocations were formed, which indicates that these structures served as barriers to dislocation movement. Microcracks along twin boundaries were detected in an irradiated specimen compressed 8.4%, but this effect was not observed in other irradiated specimens compressed up to 40%. Typical electron-transmission structures observed in unirradiated and 2×10^{18} nvt-irradiated specimens compressed to 5% reduction in thickness at 77°K are shown in Figures 33 and 34, respectively. Once again the only apparent effect of irradiation on the structures is that the unirradiated specimens contained internal dislocation sources while the irradiated specimens did not.

Internal Dislocation Sources. Additional experiments were carried out to learn more about the internal dislocation sources and their relationship to the deformation behavior of Fe. Results indicate that these structures are almost certainly due to ϵ -carbide precipitates in the Fe. No ϵ -carbide precipitates are visible in Ferrovac E after furnace-cooling from 700°C, and no "internal dislocation source" structures are produced

by straining after holding for several days at ambient temperature. However, if the furnace-cooled Fe is held for months at ambient temperature, the ϵ -carbide can apparently be precipitated by high elastic stress. Thus, it appears that some segregation of carbon in the supersaturated solid solution is necessary before precipitation can be induced by stress. The ϵ -carbides are visible as small platelets lying parallel to the $\{100\}$ planes of the Fe. After light plastic strain they appear as small patches of concentrated dislocations. After heavier plastic strain these patches interact with dislocations from other sources. Heating at 350°C for 2 hr causes the ϵ -carbides to disappear but does not remove the patches of concentrated dislocation, which indicates that the ϵ -carbides do serve as internal dislocation sources. Although the resulting dislocations do not appear to move very far from the source, they should help to distribute the initial deformation during yielding of unirradiated Fe. They might be expected to cause an increased rate of strain hardening by interfering with the motion of slip dislocations.

Fast-neutron irradiation to a fluence of 1×10^{16} nvt at 60°C causes precipitation of ϵ -carbides in Ferrovac E furnace-cooled or quenched after annealing at 700°C. The ϵ -carbides thus precipitated in Ferrovac E containing 30 ppm C and in Fe containing 100 ppm C are completely removed from the electron-transmission microstructure by a subsequent irradiation to 2×10^{18} nvt. This indicates that during the irradiation, the C in the Fe combined with radiation defects to produce complex defects in which the C atoms are bound more strongly than in ϵ -carbide. The observation also indicates that internal dislocation sources are not observed in Ferrovac E strained after irradiation to 2×10^{18} nvt at 60°C because the ϵ -carbides precipitated in the early stages of irradiation are decomposed by the subsequent irradiation because of gettering of the C by radiation defects.

Discussion. The internal friction studies of Wagenblast and Damask¹¹ and electron-transmission studies by Hull and Mogford¹² showed that C is rapidly removed from solution in Fe by fast-neutron irradiation at ambient temperature and precipitated as ϵ -carbides. It is apparent from

¹¹H. WAGENBLAST AND A.C. DAMASK, *J. Phys. Chem. Solids* 23, 221 (1962).

¹²D. HULL AND I.L. MOGFORD, *Phil. Mag.* 6, 535 (1961).

a Figure 35. Fe_3C in 0.03 wt % C-Fe. Nital etch, 1000 $\times$. (a) Unirradiated; (b) irradiated to 2×10^{20} nvt. b

these studies and from the results described above that fast-neutron irradiation to 2×10^{18} nvt at 60°C depletes the Ferrovac E iron of available C by binding the C to radiation defects. Fast¹³ and Low and Feustel¹⁴ and a number of subsequent investigators have shown that removal of available C from a relatively pure Fe promotes low fracture stress and intercrystalline fracture at low temperatures, presumably due to other impurities such as oxygen or phosphorus segregated at grain boundaries. The condition is aggravated by twinning at low temperatures due to stress concentrations where twins impinge on grain boundaries. The present results indicate that low-temperature fracture in radiation-embrittled Ferrovac E is

initially intercrystalline, and confirm that high stress concentrations exist where twins impinge on grain boundaries. The results suggest therefore that fast-neutron irradiation to 2×10^{18} nvt at reactor ambient temperature reduces the low-temperature fracture stress of Ferrovac E by depleting the Fe of available C through combination of C with radiation defects.

The electron-transmission microstructures of unirradiated and radiation-embrittled specimens of Ferrovac E after equivalent strains at 77°K show no differences that might explain the abrupt increase in the yield strength of the radiation-embrittled Ferrovac E at the ductile-to-brittle transition temperature. Crystallographic studies of these structures are in progress to seek evidence for effects of radiation on the mechanism of plastic deformation at low temperature.

¹³J.D. FAST, *Phillips Tech. Rev.* 11, 303 (1950).

¹⁴J.R. LOW AND R.D. FEUSTEL, *Acta Met.* 1, 185 (1953).

Figure 36. Electron-transmission structures of Fe_3C in 0.35 wt % C-Fe. (a and b) Unirradiated; (c and d) irradiated to 2×10^{18} nvt.

Irradiation Effects on Electron-Transmission Substructures in Iron Containing Fe_3C

Reported results of the effects of fast-neutron irradiation on the mechanical properties of irons containing the Fe_3C carbide indicate that irradiation to 2×10^{18} nvt or higher must be affecting the properties of the Fe_3C as well as those of the ferrite matrix. Since virtually all steels contain Fe_3C or stronger alloy carbides, a program has been started to look for evidence of radiation damage in such carbides by optical and electron-transmission microscopy. Initial experiments are being concentrated on Fe_3C , and are being carried out on irons containing 0.03% to 0.35% C formed by vacuum-melting Ferrovac E and adding C.

Optical examination of irons containing 0.03% and 0.35% C which had been annealed at 725°C and slow-cooled showed that Fe_3C was present in patches of relatively massive particles resulting from partial spheroidization of the cementite plates in pearlite. Irradiation to 2×10^{20} nvt had no detectable effect upon the microstructure of 0.35% C-Fe, but appeared to reduce the concentration of finer Fe_3C particles in 0.03% C-Fe,

which suggests partial decomposition of the carbides by the irradiation. This effect is shown in Figure 35. Since it could not be established that the observed difference in structures did not exist prior to the irradiation, it will be necessary to check this observation by examination of a single specimen before and after irradiation.

Specimens of 0.35% C-Fe, both unirradiated and irradiated to 2×10^{18} nvt, were examined by electron transmission. It was generally possible to distinguish Fe_3C from ferrite by a smoother surface on the Fe_3C . Typical electron-transmission microstructures are shown in Figure 36. The ferrite contained dislocations which probably resulted from stresses arising from differences in contraction between the carbides and ferrite during cooling from the annealing temperature. The carbides also contained dislocations and other interesting structures such as the bend stacking fault with "stair-rod" dislocations in Figure 36c, the unidentified "tadpoles" in Figure 36d, dislocation networks at interfaces between carbide particles, and frequent serrated interfaces between carbide and ferrite. No apparent effect of irradiation on the carbide structures was noted. In par-

ticular, no fine structure could be detected in the irradiated carbides that might be attributed to radiation damage. Experiments are in progress to determine the effects of irradiation plus strain on the carbide microstructures.

Physical and Chemical Properties of Refractory Compounds

Work in this area during 1967 included studies of the thermodynamic, electrical, magnetic, and thermal properties of refractory compounds. Investigations were continued on two types of compounds: (1) refractory thorium and uranium compounds including carbides, nitrides, oxides, borides, and phosphides, and (2) graphite lamellar compounds.

ELECTRICAL AND MAGNETIC PROPERTIES OF REFRACTORY COMPOUNDS

A. AUSKERN, S. ARONSON

Electrical Properties

During the year the electrical properties of five refractory actinide systems were investigated. Work was completed on the thorium-carbide-thorium nitride and thorium-boron systems. Work was started on the ThC-UC, ThC, ThC-“LaC” ($\text{Th}_x\text{La}_{1-x}\text{C}_y$), and ThC_xO_y systems. These systems with the exception of the borides have potential application as reactor fuels. Emphasis has so far been placed on Th rather than U because the results obtained on the Th compounds appear easier to interpret. As our understanding of the Th compounds has increased, the U analogues

have been more intensively studied. The borides represent a class of interstitial compounds that are considerably different from the carbides and nitrides. The boron atoms exist in a number of different configurations, from isolated atoms to complex, 3-dimensional networks.

Electrical properties of ThC-ThN solid solutions were found to be similar to those of non-stoichiometric thorium carbides.¹⁵ As the ratio of nitrogen to carbon increases (or as the valence electron concentration increases) the resistivity and the Hall coefficient decrease and approach the values for thorium nitride.¹⁶ The Hall coefficient is appreciably temperature dependent for all the compositions studied, which indicates that two energy bands are contributing to the conductivity. This is at variance with Piper's¹⁷ conclusions for groups IV and V refractory metal carbide and nitride solid solutions that additional valence electrons above a concentration of 8 enter a single, nearly empty energy band.

Two compounds, ThB_4 and ThB_6 , have been reported in the Th-B system. Both have metallic electrical properties. In Table 14, some of the properties of these compounds are tabulated. Hall coefficient measurements indicate a carrier concentration of 2 electrons per Th atom. This high carrier concentration is consistent with current bonding models in borides,¹⁸ which predict that both MB_4 and MB_6 should exhibit the same Hall

¹⁵A. AUSKERN AND S. ARONSON, *J. Appl. Phys.* **38**, 3508 (1967).

¹⁶A. B. AUSKERN AND S. ARONSON, *J. Phys. Chem. Solids* **28**, 1069 (1967).

¹⁷J. PIPER, in *Intern. Symp. Compounds of Interest in Nuclear Reactor Techniques*, p. 29, J. T. Waber and P. Chiotti, Editors, AIME, Aug. 1964.

¹⁸W. N. LIPSCOMB AND D. BRITTON, *J. Chem. Phys.* **33**, 275 (1960).

Table 14

Properties of Thorium Borides

Composition	Lattice parameter, Å	Density, g/cc	Resistivity* (300°K), $\mu\Omega\text{-cm}$	Hall coefficient** (300°K), $\text{cm}^3/\text{coulomb}$	Thermoelectric power (300°K), $\mu\text{V}/^\circ\text{K}$
ThB_4	$A_0=7.265$ $C_0=4.110$	7.9 (93% T.D.)	67 ± 5	-1.5×10^{-4}	-5 ± 1
ThB_6	$A_0=4.108$	5.4 (76% T.D.)	34 ± 1	-2.0×10^{-4}	-5 ± 1

*Corrected to theoretical density (T.D.) with use of the Maxwell-Euken correction.

**Corrected to theoretical density with use of $R_0 = R_m(1 - P)$.

coefficient; for a quadrivalent metal, this should indicate 2 electrons per metal atom. The thorium borides not only support the model but extend it, for the first time, to a quadrivalent metal.

Only a few measurements have been made in the ThC-UC system. This system, as well as the ThC-"LaC" system, is extremely reactive to air and moisture. Handling techniques that were successful for ThC_x have been inadequate for these systems. The resistivities of the solid solutions Th_{0.97}U_{0.03}C_x and Th_{0.92}U_{0.08}C_x are greater than the resistivity of ThC_x by about 15%.

Magnetic Susceptibility

The magnetic susceptibilities of thorium carbides, nitrides, and carbonitrides have been measured at temperatures of -190° , -76° , and 22°C . The data obtained on thorium carbides are shown in Table 15. The temperature dependence was small in all cases, although the susceptibility of the carbonitrides and the mononitride appeared to decrease slightly with increasing temperature.

In Figure 37 the room-temperature susceptibility for nonstoichiometric thorium monocarbides, carbonitrides, and mononitrides is plotted as a function of the valence electron concentration (VEC). In this type of plot, which has been extensively used in the case of transition metal carbides and nitrides, all the electrons outside the noble gas cores of the atoms are counted. The assigned valences are 4 for thorium, 4 for carbon, and 5 for nitrogen. It can be seen that the susceptibility decreases with increasing VEC in the region

Figure 37. Room-temperature susceptibility of thorium carbides, □; of nitrides, △; and of carbonitrides, ○.

of nonstoichiometric thorium monocarbides (ThC_{0.66} to ThC_{0.96}) and then increases with increasing VEC in the carbonitride and nitride region.

Two investigations of the susceptibility of thorium carbides have been reported. Bates and Unstead [*Brit. J. Appl. Phys.* 15, 543 (1964)] measured the susceptibility of thorium monocarbide, thorium dicarbide, uranium monocarbide, and solid solutions of uranium and thorium monocarbides at temperatures of 90° to 1100°K to be an order of magnitude lower than values obtained here. Satow [*J. Nucl. Mater.* 21, 343 (1967)] measured the susceptibility of several monocarbide samples and found it to decrease with increasing carbon content, in agreement with BNL data. However, both his susceptibility values and their change with carbon content are somewhat higher than ours.

Table 15

Magnetic Susceptibility Data on Thorium Carbides

Sample No.	Composition, C/Th atom ratio	Lattice parameter, Å	Susceptibility, emu/g		
			22°C	-76°C	-190°C
144	0.743	5.313	15.5	15.5	15.7
145	0.786	5.318	15.5	15.3	15.0
146	0.808	5.325	15.0	15.0	15.2
242	0.887	5.334	14.9	14.7	14.6
255	0.952	5.340	13.4	13.2	13.2
255A	0.882	5.332	14.5	14.3	14.3
253	1.469	monocarbide + dicarbide	13.7	13.6	13.7
253A	1.331	monocarbide + dicarbide	12.9	12.9	12.7
252	1.775	dicarbide + monocarbide	12.2	12.2	12.4
251	1.873	dicarbide + monocarbide	11.8	12.0	12.1
251A	1.690	dicarbide + monocarbide	12.6	12.8	13.1

Figure 38. Intensities of x-ray diffraction peaks of $\text{ThP}_{0.95}$ relative to the 620 peak at room temperature.

Analysis of the susceptibility data and comparison with the results of the electrical measurements on these compounds indicate that, whereas the electrical properties are controlled by the conduction electron concentration, the susceptibility is determined primarily by the concentration of holes in a two-band model. Both holes and electrons are present in all the various compositions studied, although the amount of band overlap varies.

CHARACTERISTIC TEMPERATURES AND ENTROPIES OF REFRACTORY THORIUM COMPOUNDS S. ARONSON, A. INGRAHAM

Characteristic temperatures for the compounds ThS , ThN , $\text{ThC}_{0.91}$, $\text{ThP}_{0.95}$, Th_3P_4 , ThO_2 , and ThB_6 were determined from x-ray diffraction peak intensity measurements. The reduction of peak intensity with increasing temperature was measured from room temperature to 1000°C . The relative intensities as a function of temperature for five diffraction peaks of $\text{ThP}_{0.95}$ are shown in Figure 38. Plots of the logarithm of the intensity vs temperature are approximately linear, in agreement with the theoretical equation

Table 16

Entropies of Thorium Compounds Calculated From the Characteristic Temperatures Determined From x-Ray Data

Compound	Calculated entropy from characteristic temperature, cal/g-atom Th-°K	Literature values, cal/g-atom Th-°K	Mean square vibrational amplitude, $\text{\AA}^2$
ThO_2	14.2	15.6 ± 0.03	0.009
ThN	12.0	12.2 ± 2	0.010
ThS	16.9	18.0	0.018
$\text{ThC}_{0.91}$	12.1	8.3 ± 3	0.012
$\text{ThP}_{0.95}$	16.6	7.8 ± 11	0.018
Th_3P_4	17.5	—	0.015
ThB_6	27.8	—	0.016

Table 17

The Heats of Reaction for the First Three Stages of the K-Graphite, Rb-Graphite, and Cs-Graphite Systems in kcal/mole of Alkali Metal

Stage	K	Rb	Cs
1	31	33.9	43.8
2	22	25.3	29.6
3	23	27.2	32.7

$$\ln \frac{I(T_1)}{I(T_2)} = \frac{n^2}{2a^2mk\theta^2} (T_2 - T_1), \quad (1)$$

in which $I(T_1)$ and $I(T_2)$ are the intensities of a diffraction peak at temperatures T_1 and T_2 , a is the lattice parameter, m is the atomic mass, k is Boltzmann's constant, θ is the Debye characteristic temperature, and $n^2 = h^2 + k^2 + l^2$, h, k, l being the Miller indices of the plane corresponding to the diffraction peak.

The entropies of the Th compounds were calculated from the characteristic temperatures determined from the x-ray data with use of Eq. (1) and are compared in Table 16 with data in the literature. The entropy values calculated from the characteristic temperatures, with the exception of those for ThO_2 , are probably more accurate than the literature values. The mean square vibrational amplitudes of the Th atoms in the lattice were also calculated from the characteristic temperatures and are presented in Table 16.

Figure 39. Knudsen effusion-electrobalance apparatus used to study the K-graphite system.

THERMAL DIFFUSIVITY A. AUSKERN

Equipment for measuring the thermal diffusivity of refractory actinide compounds by the "flash" technique is being assembled. This technique consists of irradiating the front surface of a flat, thin specimen with a very short heat pulse and then following the temperature response of the back surface. From the data obtained, the thermal diffusivity, the thermal conductivity, and the specific heat can also be calculated.

GRAPHITE LAMELLAR COMPOUNDS F. SALZANO, S. ARONSON, W. KALINOWSKI

Phase Equilibria and Thermodynamic Properties of the Potassium-Graphite Compounds

Phase equilibria in the K-graphite system were studied and shown to be similar to those in the Cs- and Rb-graphite systems. By means of a recently developed Knudsen effusion-electrobalance technique of measuring vapor pressure, the compound $C_{10}K$, analogous to $C_{10}Rb$ and $C_{10}Cs$, was found to exist in the K-graphite system.

The apparatus used for the vapor pressure measurements (Figure 39) consists of a Cahn electro-

Figure 40. A typical effusion curve taken from the recorder tracing showing the rate of emission of K from the effusion cell at 450°C.

balance, the electronic controls and recorder, a Pyrex balance enclosure, hang-down tubes, and a vacuum system. A typical effusion run is started by heating the cell rapidly to the desired temperature. K is emitted from the cell and the rate of emission is determined by continuously monitoring the weight of the cell on a recorder.

The first break in the curve in Figure 40 corresponds approximately to the composition $C_{10}K$. Thus, the first linear portion of the curve corresponds to the two-phase region

The second break in the curve corresponds to the composition $C_{24}K$, and the second linear portion of the curve corresponds to the two-phase region

Subsequently, the third linear portion, which corresponds to the two-phase region

also shows a break (not shown).

The heats of reaction for the first, second, and third stages [Eqs. (1), (2), and (3), respectively] have been calculated, and the results are shown in Table 17.

The heats of reaction for all the stages shown decrease in the order Cs, Rb, K. It is very likely that this trend continues on to Na. This could ac-

count for the low stability of Na-graphite evidenced by the inability of Na to form stages higher than $C_{64}Na$.

Reactions Between Cesium and Carbon Blacks

A study has been completed of the reactions between Cs and nongraphitic carbons. Two carbon blacks were used: an annealed (2700°C) carbon black, Sterling MT-D5; and an as-prepared carbon black, Spheron 6. Both materials were supplied by the Cabot Corp., Boston, Mass. A series of composition vs pressure isotherms was obtained at temperatures of 350° to 550°C in the composition range $C_{24}Cs$ to C_8Cs with use of experimental techniques developed previously. Entropies and heats of reaction were calculated from the data.

The maximum Cs composition achieved with the two carbon blacks studied corresponded to the formula C_8Cs , which was also the maximum composition achieved in the Cs-graphite system and has been reported by other investigators for Cs-charcoals and other Cs-lampblack materials. Thus, the composition C_8Cs is a property of carbons in general rather than of a specific crystal structure, whereas the chemical activity of Cs in these compounds is dependent on the nature of the carbon. The behavior of three Cs-carbon systems (graphite, Sterling MT-D5, and Spheron 6) is shown in Figure 41. These materials exhibit three distinctive types of isotherms. The Cs-graphite system shows two distinct two-phase regions corresponding to the vertical portions of the isotherm. The two-phase regions in the lower and upper composition range are analogous to reactions (2) and (1), respectively, in the K-graphite system. In the case of the Sterling MT-D5 carbon black, the rapidly rising portion of the isotherm in the fraction of C_8Cs composition range from 0.3 to 0.7 corresponds to a two-phase region analogous to reaction (2). The occurrence of the phase change over a range of pressures is attributed to the non-homogeneous structure of the carbon black.

An interesting feature of the Cs-Sterling MT-D5 system is that it exhibits hysteresis, while no significant degree of hysteresis has been detected in the Cs-Spheron 6 system. The hysteresis loops observed in this system and in the Cs-graphite system are interpreted to be the result of irreversible work done in the rearrangement of the graphitic layers during the phase change corresponding to reaction (1). Reaction (2) does not involve any re-

Figure 41. The behavior of three Cs-carbon systems: graphite, Sterling MT-D5, and Spheron 6.

arrangement of the graphitic layers and no hysteresis is observed. The irreversible work done in the graphite and Sterling MT-D5 systems is 27 and 80 cal/mole carbon, respectively. It is attributed to the excess free energy required to initiate the movements of regions or groups of graphitic layers interlinked by nonaromatic covalent bonds and crystal imperfections. The absence of hysteresis in the Spheron 6 system is due to the low degree of cross-linking between the graphitic layers in this untreated material.

The Reaction Between Sodium and Graphite

The reaction between Na and graphite does not take place readily, but has been reported to occur at high Na pressures. To avoid graphite deterioration in a Na-cooled reactor, it is useful to know the threshold pressure for the reaction of Na with graphite, below which no reaction occurs.

Recently it has been found that these threshold pressures can be predicted from thermodynamic data provided that the phase equilibria are known and thermodynamic data are available. Such data have been obtained here for the Cs-graphite and Rb-graphite systems, and in Table 17 data on the K-graphite system are given. However, no reliable data exist on the Na-graphite system. Therefore the threshold pressures have been calculated for this system, as well as for the K-graphite, Rb-graphite, and Cs-graphite systems for which the

Figure 42. Calculated threshold pressures for the reactions between the alkali metals and graphite.

data are known, by assuming an ionic bonding between the alkali metal and the graphitic layers.

The results are plotted vs the reciprocal absolute temperature in Figure 42. The threshold pressure increases in the order Cs, Rb, K, Na, so that initiation of the reaction between Na and graphite requires pressures >3 orders of magnitude higher than those for the other alkali metals, and of the same order of magnitude as the vapor pressure of Na. This explains the low stability of the Na-graphite compounds and the difficulty of forming Na-graphite compounds with high Na content.

Liquid State of Metals

A. PASKIN

Studies in the Liquid Metal Program have been made in the following areas: applications of the hard sphere concept to the self-diffusion, velocity of sound, and temperature dependence of the structure factors of liquid metals; experimental

Table 18

Comparison of the Calculated and Experimental Self-Diffusion Coefficients of Simple Liquids at the Melting Point

	$D_{\text{expt}} \times 10^5$	$D_{\text{calc}} \times 10^5$	$\Delta D\%$
K	3.90 ^a	3.86	-1
Na	4.05 ^a	4.2	+4
In	1.66 ^b	1.78	+7
Sn	2.05 ^b	1.92	-6
Zn	2.02 ^a	2.52	+25
Cu	3.96 ^a	3.32	-16
Pb	2.19 ^a	1.7	-22
Ag	2.55 ^a	2.8	+10
Hg	1.17 ^c	0.98	-20
Ar	1.53 ^d	1.6	+4
Li	6.5 ^e	7	+7
Ge	1.67 ^f	1.7	+2

^aN.H. NACHTRIEB, *Advan. Phys.* **16**, 309-23 (1967).

^bG. CARERI, A. PAOLETTI, AND M. VICENTINI, *Nuovo Cimento* **10**, 1088 (1958).

^cR.E. MEYER, *J. Chem. Phys.* **65**, 568 (1961).

^dG. CINI-CASTANUOLI AND F.P. RICCI, *J. Chem. Phys.* **32**, 19 (1960).

^eJ. MURDAY AND R.M. COTTS, *Bull. Am. Phys. Soc.* **12**, 359-60 (1967).

^fJ. PETIT AND N.H. NACHTRIEB, *J. Chem. Phys.* **24**, 746 (1956).

measurements and theoretical calculations of resistivities and thermoelectric powers of liquid metals and alloys; measurements of the densities of liquid alloys; studies of electromigration in liquid alloys; and studies of electrical properties of alkali metal-graphite systems.

ATOMIC AND STRUCTURAL PROPERTIES OF LIQUID METALS

A simple model has been developed to describe the atomic self-diffusion coefficient of liquid metals in terms of the Van der Waals concept of a dense fluid. The observation that all simple liquids, metallic and nonmetallic, are very similar in structure near their melting points and that the local mutual atomic arrangement can be understood as a result of packing of hard spheres suggests that the structure of liquid metals like that of insulating liquids, is largely determined by the short-range repulsive forces. Accordingly the underlying idea in the treatment is that the particles in the system are hard-spherelike and move in straight lines be-

tween core collisions. The attractive potential energy or cohesive energy term is thought of as a uniform negative potential which does not effect the basically hard sphere collisions.

By use of the Enskog hard sphere formulation the following results are obtained: (1) a relationship for the coefficient of self-diffusion which accurately gives both the magnitude and temperature dependence over the entire liquid range at atmospheric pressure; and (2) a relation between the melting point and the coefficient of self-diffusion which is the freezing counterpart of the Lindemann law of melting. In Table 18 self-diffusion coefficients calculated at the melting point are compared with measured coefficients. The same model of hard spheres immersed in a uniform background potential, which stabilizes the system, has been used to calculate successfully the velocity of sound and the compressibility in liquid metals of widely different masses, densities, and melting points. In

Table 19 calculated values of the velocity of sound at the melting point are compared with measurements. The very good agreement between calculated and measured velocities of sound near the melting point in liquid metals and the consistence of the model with a previous description of the atomic self-diffusion are cause for some confidence in the basic assumptions made. In addition, the ability to correlate sound velocity with self-diffusion coefficient by the same hard sphere radius or to eliminate the melting temperature between the two results is encouraging.

The statement was made earlier that the structures of all simple liquids are very similar. Nevertheless, a detailed comparison of the diffraction data for different liquids shows some evidence of small deviations from the common behavior.

An interesting deviation occurs in some polyvalent metals, such as gallium; it appears as a distortion of the main diffraction peak. It is not

Table 19
Comparison of the Calculated and Measured Velocities of Sound in Liquid Metals

	T_m	M	Z	$\frac{1}{5} \left(\frac{2ZE_F}{3KT_m} \right)$	$S_{B.S.}$	S_m	S_{exptl}	$\frac{S_{exptl}}{S_m}$	$KT_m \rho X_T$
Na	373	23	1	13.2	2960	2500	2526	1.01	0.025
K	338	39.1	1	9.2	1810	1720	1890	1.1	0.028
Rb	313	85.48	1	8.6	1140	1103	1260	1.12	0.028
Cs	303	132.91	1	8.5	880	890	967	1.03	0.028
Cu	1356	63.54	1	8.2	2580	2700	3460	1.28	0.0285
Ag	1233	107.88	1	6.6	1740	1920	2710	1.4	0.0297
Zn	693	65.6	2	42.5	4180	2610	2712	1.02	0.014
Cd	594	112.41	2	40.5	2850	1840	2166	1.17	0.015
Hg	235	200.61	2	103	2100	1220	1478	1.2	0.008
Al	934	26.97	3	46	8750	4900	4670	0.96	0.014
Ga	303	69.72	3	168	5430	2850	2873	1.01	0.005
In	429	114.82	3	95	3760	2041	2315	1.11	0.008
Tl	575	204.4	3	66	2760	1580	1625	1.03	0.011
Sn	505	118.70	4	128	4630	2440	2464	1.02	0.006
Pb	601	201.21	4	100	3350	1900	1776	0.94	0.008
Sb	903	121.76	5	112	5340	3150	1893	0.6	0.006
Bi	544	209	5	146	3940	2080	1649	0.8	0.007

The experimental data were taken by R.T. Smith et al., *Advan. Phys.* **16**, 515 (1967). S_m is the calculated velocity of sound at the melting point according to the formula

$$S_m = \left\{ \frac{KT_m C_p}{M C_v} \left[27 + \frac{1}{5} \left(\frac{2ZE_F}{3KT_m} \right) \right] \right\}^{1/2}$$

C_p/C_v has been taken equal to 1.15 for all metals, ρ is the mean atomic density, E_F is the Fermi energy, X_T is the isothermal compressibility, $S_{B.S.} = (2ZE_F/3M)^{1/2}$ is the Bohm and Staver result for the velocity of sound [D. Bohm and T. Staver, *Phys. Rev.* **143**, 36 (1966)], T_m is the melting temperature, M the atomic mass, and Z the valence.

known whether this distortion is mainly a molecular effect like that due to a strong atomic bond, as occurs in biatomic insulating liquids such as liquid bromine, or whether it is a many-body electron effect directly reflected in the interatomic forces which then affect the liquid structure. V. Heine (in *Battelle Colloquium on Phase Stability*, McGraw-Hill, New York, 1966) has recently suggested that an effect of the latter type occurs in polyvalent metals. It was decided that an independent check of this argument could be obtained more directly from neutron inelastic scattering data of liquid polyvalent metals, because these data can be more closely related to the interatomic forces in the wave vector space representation. At present it can be concluded that the gross features of the structure of liquid metals and related atomic properties are mainly determined by the short-range repulsive part of the interatomic forces. A complete explanation of the details of properties such as the temperature coefficients of the velocity of sound and the distortions of the structure factors must await better understanding of the volume and temperature dependence of the interatomic forces in general and of the long-range attractive forces in particular.

P. ASCARELLI, A. PASKIN

THE HARD SPHERE MODEL AND TEMPERATURE-DEPENDENT PROPERTIES RELATED TO STRUCTURE

The work of Ashcroft and Lekner [*Phys. Rev.* 145, 83 (1966)] indicated that the structure factors, $a(K)$, for most metals at their melting points are well described by a simple hard sphere model except for the region of K below the first peak. Ascarelli and Paskin (see previous section) showed subsequently that the hard sphere equation of state, when modified by a Van der Waals term, can give accurate values of the self-diffusion coefficient and its temperature dependence. An investigation has now been undertaken to discover the extent to which the hard sphere concept can be applied to short-range properties other than diffusion, to long-range properties such as compressibility or velocity of sound, and to properties that are dependent on both the short-range or repulsive part of the interatomic forces and the long-range or attractive part, i.e., the structure factor $a(K)$, and through it the electron transport properties.

The calculation of the temperature dependence of a liquid-metal diffraction pattern has given the most encouraging result. Few diffraction experiments have been performed as a function of temperature, but, where comparison is possible, the agreement is good out to the third or fourth peak. The closeness of the agreement is indicated in Table 20, in which the first peak intensities of liquid Rb and In are compared at various temperatures. The significance of the agreement out to large values of K on the r -space distribution is being investigated.

The variation of $a(K)$ in the long-wavelength limit has also been studied in terms of the isothermal compressibility, χ_T , i.e., $a(0) = kT\chi_T\rho$, where k is the Boltzmann constant and ρ is the number density. For the alkali metals, it was found that the absolute value and temperature dependence of χ_T was given by the hard sphere interaction, but this was not the case for the polyvalent metals. However, the inclusion in the equation of state of a term arising from the presence of an electron gas resulted in good values for the compressibilities of the polyvalent metals. The velocity of sound, U , is related to the compressibility by the well-known relation

$$U^2 = \frac{1}{M\chi_T\rho} \frac{C_p}{C_v},$$

where M is the particle mass. The values calculated for Rb, Zn, In, and Sn (see Table 21) are

Table 20

Comparison of the Experimental and Calculated Values of the First Peak Intensity of the Structure Factors of Liquid Rubidium and Indium

Rubidium			Indium		
T, °C	1st Peak Intensity		T, °C	1st Peak Intensity	
	Exptl*	Calc		Exptl*	Calc
40	2.56	2.52	170	2.486	2.465
160	2.09	2.03	280	2.056	2.124
240	1.98	1.82	390	1.841	1.897
360	1.81	1.61	500	1.747	1.736
			650	1.565	1.577

*The experimental values for Rb are from Gingrich and Heaton [*J. Chem. Phys.* 34, 873 (1961)]; those for In are from Ocken and Wagner [*Phys. Rev.* 149, 122 (1966)].

Table 21

Comparison of the Velocity of Sound and
Its Temperature Coefficient at the Melting Point
for Several Metals

Metal	Velocity at mp, m/sec		Temperature coefficient	
	Exptl	Theory	Exptl	Theory
Rb	1260	1103	0.4	0.85
Zn	2712	2610	0.305	0.75
In	2315	2041	0.5	0.4
Sn	2480	2440	0.3	0.4

The experimental values are taken from Gitis and Mikhailov [*Soviet Phys. Acoust. English Transl.* **12**, 131 (1966)] and Smith et al. (in *Properties of Liquid Metals*, P.D. Adams et al., Editors, Taylor & Francis, London, 1967).

Table 22

Comparison of the Temperature Coefficient of Resistivity
for Various Metals Near the Melting Point

	$\partial\rho/\partial T \times 10^8$ ohm-cm/ $^{\circ}\text{C}$	
	Exptl	Calc
Na	3.59	3.96
Rb	8.64	9.73
Cd	0	-0.78
Zn	-0.85	-0.87
In	2.55	2.82
Sn	2.76	3.30

typical of the results obtained. The agreement with experiment is reasonably good for both the absolute values and the temperature dependence, given the simplicity of the model. A much better understanding of the volume and temperature dependence of the long-range interaction is required before closer agreement with experiment can be expected.

It is thus possible to calculate reasonable values of much of the $a(K)$ curve required to determine the electron transport properties. The values between $a(0)$ and the first peak, where the long-range attractive part of the interatomic forces is of importance, await a fundamental physical interpretation, which is still under study. However for the purpose of calculating the electron transport properties, an empirical means of determining $a(K)$ in this region is of value. The simple hard sphere form provides sufficient agreement with the

experimental diffraction curves of the alkali metals, while the other metals, for which $a(0)$ has been modified to give the experimental velocity of sound, require an interpolation between the $a(0)$ value and the peak given by the hard sphere form. Various functions were used to determine the best fit to the temperature dependence of $a(K)$ in the low K region for liquid In. The best form turned out to be close to a step function, which was then used for other metals.

With this calculated $a(K)$ and a simple form of pseudopotential [N.W. ASHCROFT, *Phys. Letters* **23**, 48 (1966)], adjusted to give the experimental resistivity at the melting point, the temperature dependence of resistivity for several metals has been calculated. The results are presented in Table 22. A notable success is the calculation of a negative temperature coefficient of resistivity for liquid Zn. When the inaccuracies associated with the pseudopotential method are considered, the agreement with experiment is quite remarkable.

The thermoelectric power provides a sensitive test of the volume dependence of the pseudopotential. With the exception of Na and K, the agreement with experiment is not good. In the case of these two metals a somewhat fortuitous agreement arises because the contribution to the thermopower from the pseudopotential is small. It has become evident that, until the volume dependence of the pseudopotential is better understood, reasonable values of thermopowers should not be expected.

P. ADAMS, P. ASCARELLI

THE BORN APPROXIMATION AND RESISTIVITY THEORY

The validity of using the Born approximation result in the calculation of electron transport properties has been recently questioned by Greenfield and Wiser (in *Properties of Liquid Metals*, P.D. Adams et al., Editors, Taylor & Francis, London, 1967). The value of the temperature coefficient of resistivity, α , unlike that of the resistivity itself, is fairly insensitive to the choice of pseudopotential and thus provides a means of testing the assumptions behind the resistivity formula. The objection to the Born approximation was based on the observation that α_{calc} , determined from the change with temperature of the experimental x-ray diffraction pattern of liquid Na and any reasonable pseudopotential, was about a factor of 2 less than α_{exptl} . However, an investigation of the experimental

errors in the diffraction experiment reveals that the evidence supporting the value of α_{calc} is by no means conclusive. Moreover, although the α_{exptl} chosen was $0.0040/^{\circ}\text{C}$, the literature contains values down to $0.00344/^{\circ}\text{C}$, a variation of 14%. This will have a significant effect on the ratio $\alpha_{\text{calc}}/\alpha_{\text{exptl}}$.

The value of α_{exptl} has now been carefully re-determined in the same temperature range as that used for the x-ray experiment. The value obtained is $0.00367/^{\circ}\text{C}$, which leads to values of $\alpha_{\text{calc}}/\alpha_{\text{exptl}}$ in the range 0.65 to 0.80. Since this ratio is now approaching unity, it must be concluded that the x-ray data for liquid Na do not provide an unambiguous test of the Born approximation formula for electrical resistivity.

P. ADAMS

ALLOY RESISTIVITIES

The alloys of mercury with polyvalent metals are characterized by a rapid decrease in resistivity from the pure Hg value with increasing concentration. This property is in strong contrast to the conventional behavior of binary alloys. It has been suggested by Mott [*Phil. Mag.* 13, 989 (1966)] that the unusually large resistivity of pure Hg and its rapid decrease with solute concentration is associated with a minimum in the electron density of states in the vicinity of the Fermi surface. It was proposed that the addition of polyvalent solute caused the Fermi level to move away from this minimum, which increased the density of states at the Fermi level and consequently decreased the alloy resistivity. A further consequence of this qualitatively reasonable model is that the addition of a nonalkali monovalent metal to Hg would cause the Fermi level to move toward the density

of states minimum, with a corresponding increase in alloy resistivity.

The resistivities of Hg-Au alloys have now been measured and show the same rapid decrease with Au concentration as that exhibited by Hg-Sn alloys. This is in contradiction to the result expected on the Mott model. It can be seen that the model is not a reasonable explanation of the properties of Hg by plotting the conductivity of the alloys as a function of Fermi energy (Figure 43). The variation of conductivity with Fermi energy for pure Hg is linear, which shows clearly that, within the framework of the Mott model, changing the temperature does not cause the Fermi level to move through a deep minimum in the density of states. This being the case, the conductivity should behave in a similar manner when the Fermi energy is decreased by adding Au to Hg at constant temperature. The fact that the conductivity increases

Figure 43. The variation of electrical conductivity with Fermi energy for pure Hg as a function of temperature and for Hg-Au alloys at 200° and 300°C.

Figure 44. Electrical resistivities of Na-Cd alloys at 325°C.

Figure 45. Electrical resistivities of Sn-Cd alloys at 325°C.

with decreasing Fermi energy indicates that, even if a minimum in the density of states exists, it does not play a significant role in the resistive properties of liquid Hg and its alloys.

Although it has been demonstrated that the unmodified hard sphere form of the structure factor, $a(K)$, is in serious error for small values of K , it is still reasonable to use this form in the calculation of the resistivities of binary alloys. This is so because, in the region of error, $a(K)$ is of the order of 0.02, while the variation of resistivity with composition depends largely on the factor $1 - a(K)$.

The calculations for Na-Cd and Sn-Cd are shown in Figures 44 and 45. The hard sphere ratio σ_A/σ_B is assumed to remain constant, and the packing fraction, η , to vary linearly between the pure metal values. Over the range of composition for which these calculations can be compared with experiment the agreement is good, and work is being continued to allow comparison at all compositions.

The results on Hg-Sn are presented in Figure 46. The conventional pseudopotential calculation results in a fairly rapid decrease in resistivity with increasing Sn concentration without any assumptions as to the effect of a minimum in the density of states. The calculated resistivity decrease of Hg-rich alloys is still much smaller than the observed decrease, and this is attributed to a rather large energy dependence of the Hg pseudopotential which has not yet been taken into account.

These results indicate that the hard sphere approach is reasonably successful in the calculation

Figure 46. Electrical resistivities of Hg-Sn alloys at 232°C.

of alloy resistivities, and work is continuing to determine the extent to which other properties can be approximated by the hard sphere concept.

P. ADAMS, S. FINK, C. POSPISIL

THERMOELECTRIC POWER OF DILUTE SODIUM ALLOYS

An apparatus was built for measuring thermoelectric power by the small ΔT technique. The data obtained on pure Na with this technique agree closely with those of other workers using the more precise large ΔT method. Therefore the small ΔT method was selected for alloy work to avoid segregation problems. Results have been obtained on dilute alloys of Ag, Cd, In, Sn, and Sb with Na. Within the limits of error the thermopowers are linear functions of temperature up to about 460°C, the maximum working temperature. The variation of thermopower with solute concentration at 325°C is illustrated in Figure 47.

A critical test of the thermopower formula obtained from simple pseudopotential theory can be made by comparing values of q , which contains the structure factor and pseudopotential values at the Fermi level and the resistivity integral, and can be written in terms of the dimensionless thermoelectric power parameter, ξ , as $\xi = 3 - 2q$. For very dilute alloys it is assumed that the solute structure factor is unity, so that the cross partial structure factor is equal to that of pure Na. The

Figure 47. Absolute thermopower-composition isotherms at 325°C for dilute Na-based liquid alloys.

values calculated by using the Ashcroft pseudopotential and the Heine-Animalu pseudopotential are compared with the experimental results in Table 23. The results obtained with the Heine-Animalu form agree quite well with the experimental values, although the detailed changes of q with solute, particularly for In, are not found. This could arise from the large negative excess volume of mixing associated with Na-1 at. % In and a resultant significant change in the alloy structure.

H. DAVIES, A. MINARDI

DENSITY AND SOLUBILITY STUDIES

The densities of Na-In and Na-Sn have been measured up to $\approx 430^\circ\text{C}$ with use of the maximum bubble pressure technique. As in the case of the Na-Cd system discussed last year, the dependence of density on temperature is linear. The dependence on concentration at 350°C is illustrated in Figure 48. The results indicate that there is little excess volume of mixing in the Na-Sn system, while the Na-In system shows a significant negative excess volume.

The determination of liquidus temperatures and thermodynamic properties by means of solubility studies is continuing. In addition to the Na-In system, for which results have already been reported, the Na-Sn and Na-Sb systems have been examined. Analysis of the data awaits a report on the chemical compositions. H. DAVIES, A. MINARDI, S. FINK, P. ADAMS

ELECTROMIGRATION IN LIQUID ALLOYS

In last year's report, a model was proposed that offers a semiquantitative explanation for electromigration in liquid alloys. As a first approximation,

Table 23

Experimental and Theoretical Values of q ,
the Thermopower Parameter

Composition	Calc (Ashcroft)	Calc (Heine-Animalu)	Exptl
Pure Na	0.004	0.16	0.15
Na-1 at. % Ag	0.082	0.175	0.156
Na-1 at. % Cd	0.064	0.147	0.18
Na-1 at. % In	0.131	0.186	0.25
Na-1 at. % Sn	0.175	0.21	0.23
Na-1 at. % Sb	0.104	0.131	0.114

the resistivities of the pure components are taken as a measure of their scattering cross sections in the alloy, and the component with the greater resistivity should be preferentially transported to the anode.

Following this model, the electric mobility (velocity per unit field), commonly used to express electromigration rates, is not a valid parameter. Instead, the atom motion should be related to the current flow, as in the following expression:

$$J_i = P_i N_i J_e,$$

in which J_i is the solute atom flux across the capillary orifice, P_i is a proportionality constant which is a probability of electron drag, N_i is the solute atom fraction, and J_e is the electron flux. By maintaining the proper experimental conditions to prevent back-diffusion across the capillary orifice, the "coefficient of electron drag" can be obtained by use of the expression

$$P_i = \frac{n_i}{N_i n_e},$$

where n_i is the number of solute atoms crossing the capillary orifice and n_e is the number of electrons passing through the alloy in the same time interval.

Figure 48. Concentration dependence of the density of some Na-Sn and Na-In alloys at 350°C .

The electric mobilities of the several solutes in liquid bismuth previously measured have been converted to values of P , which are plotted in Figure 49 as a function of temperature. An apparently linear relationship is found, whereas the temperature dependency of the electric mobilities had been expressed as $\log U$ vs $1/T$ and had apparently satisfied the Arrhenius rate equation. The present model does not consider electromigration to be an activated process.

Angus et al. [*Met. Soc. Conf.* 7, 447-60 (1961)] had previously suggested that the component with the smaller atomic mass concentrates at the cathode. This relationship is valid for all the alloys measured in this program, although the mass effect is believed to be merely a coincidence, since in all the alloys studied the component with the greater atomic mass also has the greater resistivity and hence migrates to the anode.

To avoid this coincidence and demonstrate the correctness of our model, measurements were made with Pb-Sb alloys, since Pb is heavier than Sb but has a smaller resistivity. Electromigration was measured in Pb containing about 1 at. % Sb and in Sb containing about 1 at. % Pb by the capillary reservoir technique described in previous

Figure 49. Temperature dependences of the coefficients of electron drag for several solutes in liquid Bi.

reports. Migration of Sb in Pb was determined by using radioactive Sb, but migration of Pb in Sb had to be studied by using less precise wet chemical techniques. The results (Figure 50) show that Sb is transported to the anode, displacing Pb to the cathode, as predicted by our electron drag model, but in violation of Angus's mass criterion.

In Figure 51, all the available reliable data have been converted from values of U to values of P and are plotted as a function of the resistivity difference between solvent and solute. In every alloy the direction of relative motion is correctly predicted; Pb and Tl do not separate from Hg and have resistivities very nearly that of Hg. There is a fairly linear relationship between the amount of electromigration in an alloy and the resistivity difference of the two components, especially in polyvalent metals.

Although the migration direction is still predictable in the case of monovalent metals, there is poor quantitative correlation with the results for polyvalent metals. For example, values of P for Cu and Ag in Bi are much lower than their respective values of $\Delta\rho$ would indicate. For electromigration in liquid Na, the effect is pronounced. It was reported last year that Cd and In in liquid Na migrated toward the anode, in conformation with our model. Calculated values of P for Cd and In in liquid Na are plotted against temperature in Figure 52. Comparison of these results with those in Figure 49 shows the migration in Na to be about 5 times the respective migration in Bi, even

Figure 50. Temperature dependences of the coefficients of electron drag for dilute additions of Pb in Sb and Sb in Pb.

though Cd and In have resistivities only slightly larger than that of Na, but much smaller than that of Bi.

It was at first thought that the large values of P for Cd and In in Na stemmed from the presence of compounds in the liquid state. The compounds NaCd_2 and NaIn are known to exist in the solid state. However, preliminary results with Ag, which does not form compounds with Na, indicate nearly as large values of P in liquid Na.

S. EPSTEIN, J. RUTHERFORD

Alkali Metal-Graphite Systems

Interest in alkali metal-graphite materials stems from the question of the two-dimensionality of the alkali metal between the planes of carbon atoms. Of particular importance is the form of the melting transition. Some measurements have now been made of the electrical resistivity in the a -axis direction of potassium graphite. Two effects of interest have been observed.

1. The resistance-temperature relation between about -250°C and 400°C is composed of several linear regions. The temperature coefficient of resistance in each region is larger with increasing temperature, and the transition from one region to another is quite sharp. Some hysteresis in the heating and cooling cycles is also observed.

The results obtained so far do not indicate the existence of a well-defined order-disorder transition of the K atoms within a plane. The reason for the discontinuities in the temperature coefficient

is not clear. If, as seems likely, they are related to a change in the number of planes ordered with respect to each other, then the alkali metal in these systems must be considered three- rather than two-dimensional.

2. The resistance of K-graphite, with a nominal composition C_8K , prepared at 250°C decreases by a factor of 3 when annealed at $\approx 400^\circ\text{C}$. No explanation of this phenomenon is available at present. It could result from the ordering of K in each plane, or the intriguing possibility arises that the presence of K enables the graphite structure to become more ordered. This observation will be further investigated.

P. ADAMS, F. SALZANO

Superconductivity

A. PASKIN, D. SCHWEITZER

Studies in superconductivity represent a combined effort of the Nuclear Engineering, Physics, and Accelerator Departments. Only the portion sponsored by the Nuclear Engineering Department is reported here. It includes work on hysteresis in superconductors, studies at temperatures below 0.1°K , and superconductivity in thin films.

HYSTERESIS IN SUPERCONDUCTORS

Work completed in the past year has shown that pinning models and critical state concepts cannot account for many properties of type II superconductors. The experiments are consistent with the explanation that the hysteretic state is a new superconducting phase which has properties analogous to those of conventional solutions. In the

Figure 51. Coefficients of electron drag for various solutes in several liquid metals plotted as a function of the resistivity difference between solvent and solute.

Figure 52. Temperature dependences of the coefficients of electron drag for Cd and In in liquid Na.

hysteretic superconductor the magnetic induction B behaves as a solute. The emphasis in the present studies is on experimentally testing various implications of this explanation and justifying, from thermodynamic concepts, the existence in principle of new superconducting phases in both type I and type II superconductors. The pinning and critical state models are based on observations that retained fields in hysteretic superconductors exist in the form of gradients. A gradient in magnetic induction is equivalent to both a magnetic force and a persistent current. In pinning models it is assumed that the gradient originates in an interaction between defects and flux lines. The magnetic force generated by the gradient is assumed to balance the force exerted by the defect. In such models the interaction between flux lines and defects is the origin of the "critical" or maximum currents carried by hysteretic superconductors. In type II superconductors exhibiting appreciable diamagnetism, the gradients are confined to surface regions and a large component of the retained field is uniformly dispersed through the bulk of the solid. This configuration is analogous to the equilibrium configuration of a solution in which the solute is dispersed uniformly through the bulk and exists in the form of gradients at the surface.

The origin of equilibrium gradients in solutions can be explained by surface energy considerations and activity coefficient concepts. For a two-component system the Gibbs free energy of a surface is

$$G^s = \sigma A + n_1 \mu_1 + n_2 \mu_2, \quad (1)$$

where σ is the surface tension, n is the number of moles, and μ is the chemical potential of the components (1 and 2) in the surface. At equilibrium $dG^s = 0$ and $\sum \mu_i dn_i = 0$, so that

$$A d\sigma + n_1 d\mu_1 + n_2 d\mu_2 = 0 \quad (2)$$

or

$$d\sigma = -C_1 d\mu_1 - C_2 d\mu_2 \quad (3)$$

where the concentration $C = n/A$. Choosing the surface plane so that the solvent concentration $C_2 \rightarrow 0$, $d\sigma = -C_1 d\mu_1$. At equilibrium the chemical potential of the solute must be the same in the surface and in the bulk, $\mu_1^s = \mu_1^B$ and $d\mu_1^s = d\mu_1^B$, so that

$$C_1^s = - \left(\frac{\partial \sigma}{\partial \mu_1^B} \right)_T. \quad (4)$$

Expressing the chemical potential in terms of the mole fraction N and activity coefficient γ ,

$$\mu_1^0 = RT \ln N_1^B + RT \ln \gamma_1^B \quad (5)$$

or

$$d\mu_1^B = RT d \ln \gamma_1^B N_1^B. \quad (6)$$

Substituting Eq. (6) in Eq. (4), the surface concentration can be related to the bulk mole fraction through

$$C_1^s = - \frac{1}{RT} \left(\frac{\partial \sigma}{\partial \ln \gamma_1^B N_1^B} \right)_T. \quad (7)$$

Since the bulk equilibrium mole fraction N_1^B is different from the surface equilibrium mole fraction N_1^s , the activity coefficient in the surface differs from that in the bulk. The activity coefficient is determined by the localized forces exerted upon the solute by the surrounding medium. In the surface the forces are not symmetrical and the concentration must adjust to maintain a constant chemical potential. The nature of the equilibrium gradient required to form a constant chemical potential will be determined by the nature of the forces and their change with distance. It will take a finite number of atom layers for solute near the surface to experience the same forces as solute in the bulk. The gradient is then determined by the variation of the surface energy with concentration.

In the superconductor the magnetic chemical potential is $\partial G / \partial B$, and the analogous equilibrium condition is that the surface gradient will depend upon the variation of the surface or interface energy with the induction. Since the maximum gradient of magnetic induction determines the critical current, this condition requires $J_c = f(B)$. Another difference between a pinning model and a solution model is that in the first case the retained field is immobile or locally pinned, while an equilibrium model implies that the internal field lines are mobile. Changes in retained field with temperature have been described elsewhere for type II hysteretic superconductors exhibiting appreciable diamagnetic behavior initially and with field reversals.

In these systems, retained fields in $H=0$ formed by cycles involving one sense of H decrease with increasing temperature. When cycles involving both senses of the applied field are used, it is possible to obtain states that do not change with temperature over finite temperature regions. With a sufficient increase in temperature the retained field is then expelled with a well-defined temperature dependence. This relatively simple behavior is associated with diamagnetism and is not observed in materials that do not exhibit appreciable diamagnetism. In such materials, retained fields

formed from both senses of H go through maxima with increasing temperature. The temperature changes of retained fields in vanadium exhibiting diamagnetism and in vanadium heat-treated in such a manner that the diamagnetic behavior is removed are shown in Figures 53 and 54. In Figure 53 the temperature changes of retained fields resulting from three general types of cycles are shown for the vanadium exhibiting diamagnetism. The upper curve corresponds to the changes in retained field where the net polarity is the same as that of the field applied initially. The data falling on the zero moment line were obtained by choosing an initial cycle leading to an average value of $M=0$ for $H=0$, as shown in the insert. The lower curve denotes the changes after a cycle that produced a retained field with net negative polarity (polarity opposite to that of the field applied initially). The changes for corresponding cycles in the vanadium without diamagnetism are shown in Figure 54. In this case the initial state in which $M=0$ when $H=0$ does not correspond to a state in which no flux exists in the superconductor, but is a state in which the internal field exists with both polarities simultaneously. Upon heating, the fields corresponding to the negative polarity are expelled preferentially, which leads to an increase in positive magnetization. The results are consistent with the explanation that the internal fields in superconductors exhibiting diamagnetism exist with only one polarity present; i.e., flux annihilation is quantitative.

Since much of the retained field in the diamagnetic sample is uniformly dispersed in the bulk, the annihilation of flux is not restricted to surface regions but implies a mobility of the internal field that is not evident in the vanadium without diamagnetic behavior.

Hysteresis, field gradients, and the existence of new superconducting phases can be accounted for by the assumption that the magnetic induction changes the surface and interface energies of metals when they enter the superconducting state. The Gibbs free energy function for any finite material includes a surface term and, if the material is polycrystalline, interface terms which are small relative to the other terms. These terms are either ignored in theories dealing with infinite superconductors or are, by omission, implied to be exactly equal in both the normal and superconducting states. However, if the magnetic induction causes a change in their values in only the super-

Figure 53. Changes in retained fields (for $H=0$) with increasing temperature for vanadium exhibiting diamagnetism. The manner in which the states were formed is shown schematically by the cycles in the insert.

Figure 54. Same measurements as those shown in Figure 53 for vanadium without diamagnetism. Sample is a 30-mil-diam cylinder $\frac{1}{2}$ in. long.

conducting state, these changes may be appreciable relative to the extremely small term $G_n - G_s$ for the condensation reaction.

The justification for assuming a unique superconducting state is based on the assumption that the Gibbs free energy is given by

$$G = U - TS - HM. \quad (8)$$

The Gibbs free energy function therefore requires that the superconducting state be described by the two independent variables H and T . The phase rule for the reversible type I superconductor is

$$F = C - P + n, \quad (9)$$

where n is the number of independent variables. At the phase boundary, where the normal and superconducting phases are in equilibrium with the external field, there are two components (the magnetic field, H , and the solid material) and three phases (normal, superconducting, and the external phase, i.e., the field). If there are only two independent variables ($n = 2$), there can be only one degree of freedom (i.e., there is a single curve in the H_c vs T plane).

However, if the magnetic induction, B , changes the surface and interface energies in the superconducting state, then the Gibbs free energy of the superconducting state is given by

$$G = U - TS - HM + A_s \gamma_s + \sum_i A_i \gamma_i, \quad (10)$$

where γ_s and A_s are the geometric surface energy and area, and γ_i and A_i are the interface energies and areas associated with grain boundaries in polycrystalline materials. The surface and interface energies can be treated as independent variables, since they can be changed by changing the geometry and the polycrystalline nature of the sample. In any superconductor in which these terms are not neglected, the phase rule relation is now $F = C - P + 3$. Since it is known from experience that a single curve still exists in the H_c vs T plane, there is again only one degree of freedom. Therefore the inclusion of the surface and interface energy terms in the phase rule requires that a new phase exist. The assumption that the surface and interface energies are functions of the magnetic induction, B , leads to a term in the Gibbs free energy equation which is the magnetic analogue of the chemical potential term for a solution, where the magnetic induction, B , behaves as the solute concentration.

Define the volume average, γ_0 , of the surface and interface energies,

$$A_0 \gamma_0(B) \equiv A_s \gamma_s(B) + \sum_i A_i \gamma_i(B). \quad (11)$$

Then

$$A_0 d\gamma_0(B) = A_s \left(\frac{\partial \gamma_s}{\partial B} \right)_T dB + \sum_i A_i \left(\frac{\partial \gamma_i}{\partial B} \right)_T dB, \quad (12)$$

and from Eq. (10),

$$\begin{aligned} \left(\frac{\partial G}{\partial B} \right)_{H,T} &= A_0 \left(\frac{\partial \gamma_0}{\partial B} \right)_T \\ &= A_s \left(\frac{\partial \gamma_s}{\partial B} \right)_T + \sum_i A_i \left(\frac{\partial \gamma_i}{\partial B} \right)_T. \end{aligned} \quad (13)$$

Therefore

$$[dG]_{H,T} = \mu_B dB, \quad (14)$$

where we define

$$\mu_B \equiv \left(\frac{\partial G}{\partial B} \right)_{H,T}. \quad (15)$$

The above treatment is equivalent to replacing the independent variable γ_0 by the independent variable B . The thermodynamic definition of one independent variable with respect to the other independent variables, H and T , is

$$\left(\frac{d\gamma_0}{dH} \right)_T = \left(\frac{d\gamma_0}{dT} \right)_H = 0.$$

For $\gamma_0 = aB^M + c$, the above condition reduces to

$$\left(\frac{dB}{dH} \right)_T = \left(\frac{dB}{dT} \right)_H = 0$$

for both $B = 0$ and $B \neq 0$. The experimental properties of hysteretic superconductors satisfy this condition.

In this frame of reference the actual properties of a hollow cylinder in which the finite wall is a reversible type I superconductor are considered. The magnetization curves of these systems are well known. By accounting for the self-inductance, the magnetization can be explained by a microscopic description of how the supercurrents vary and depend upon the applied field and the field trapped in the void. In the absence of additional information such a microscopic description does not determine whether the system is or is not thermodynamically stable. After exceeding the critical field H_c and then reducing the applied field, the hollow cylinder exists in a state in which,

in the void, the internal field (which is not an independent variable) is greater than the external field. The finite shell is presumed to be completely diamagnetic (except for the penetration depths on both surfaces). In the microscopic model, therefore, the inside surface is at a higher free energy than the outside surface.

In a solution model no free energy gradient through the wall is permissible. In order that the superconducting wall may have a constant free energy throughout, the system, when going through the normal to superconducting transition with field, can spontaneously generate a new phase which retains field in the wall and in which the free energy is a function of induction or "solute concentration." Under these conditions it is permissible for the solution phase, in the presence of a high field, to have the same chemical potential as the diamagnetic phase in a lower field.

Although the superconducting wall may behave reversibly when the cylinder is split lengthwise, in the continuous geometry it should retain magnetic induction when the external field is decreased from $H = H_c$ to $H = 0$. The magnetization of the wall itself, in the continuous geometry, can be determined by measuring the field in the void at the same time that magnetization measurements of the total system are made. Such measurements were made in cylinders of 99.999% Pb, 99.999% In, and 99.99% Sn. In all cases the wall in the continuous geometry retained large internal fields and the materials were highly reversible when the

cylinders were slit along the length. An arbitrary example of the field in the wall of a particular Pb cylinder obtained from the simultaneous measurements just described is shown in Figure 55, where it is compared with the highly reversible magnetization curve obtained when the wall was cut along the length.

Consider the properties expected when the hollow cylinder is cooled from above T_c to temperatures below T_c in static external fields. In the conventional frame of reference, the Meissner effect should be the same whether the cylinder is continuous or split. In an equilibrium model, the superconducting phase with internal fields can exist in states in which the chemical potential is the same as that of the diamagnetic phase. An equilibrium configuration can be obtained where some field is retained, and this will produce a reduced Meissner effect. However, if the new superconducting phase attempts to reach its lowest free energy value it can coexist in equilibrium with the diamagnetic state only if it spontaneously creates a field inside the shell that is greater than the applied field (i.e., its own vapor pressure). Since the internal field can be built up only by expulsion into the void of the magnetic induction originally present in the wall at the transition temperature, a balance will be obtained between the two opposing processes, i.e., the tendency to retain induction in parts of the wall and the necessity to build up the internal field from flux expelled by the wall. Thus, in the solution model these systems are intrinsic flux pumps. The present measurements of fields in the void obtained after cooling from above T_c in static fields were made in Pb and Sn cylinders varying in length from 500 to 2000 mils for 15, 20, and 100-mil-thick wall cylinders with inside diameters of 150 mils. Measurements were made at final temperatures above and below the lambda point of helium. The results for the thin-wall cylinders show that the fields built up inside the cylinders are $\approx 30\%$ greater than the applied field in Sn (Figure 56) and $\approx 15\%$ greater in Pb (Figure 57). Just as the final equilibrium state of an undersaturated solution is thermodynamically constrained by the amount of solute available, the final state of the hollow cylinder with an arbitrarily thin wall is restricted by the amount of magnetic induction available in the wall when it becomes superconducting with temperature in a field. If this constraint is removed through a sufficient increase in the ratio of wall to void volume,

Figure 55. Average value of the field within the wall of a continuous hollow cylinder when the external field is reduced from H_c to 0, compared with the magnetization curve of the slit cylinder.

equilibrium requires that the same final state will be approached whether the transition from the normal state occurs by decreasing T in constant H or by decreasing H at constant T . Thus, the change in the behavior demonstrated in Figures 56 and 57 with increasing wall thickness is predictable. The enhancement in internal field will increase and the plateau will extend to lower fields. The results for the 100-mil-wall Pb cylinder shown in Figure 58 provide confirmation of these effects.

By considering the normal-to-superconducting transition in a constant external field when the temperature is lowered, it appears that there is a reasonable mechanism available to the hollow cylinder to expel the field in the wall without en-

hancing the field in the void. At the transition temperature in an applied field, the field in the void is the maximum value (H_c) that will allow the superconducting state to exist. The wall is at the point of beginning to undergo a first-order phase transition into the pure (diamagnetic) superconducting state. As heat is removed from the wall in the cooling process, the wall will *isothermally* expel flux without changing its temperature. Any small increment of flux pumped into the void during this isothermal transition will raise the field above H_c , which will instantaneously drive the wall completely normal and allow the field in excess of H_c to leak out of the void. If there were no driving force to retain field in the wall, the total field present in the wall would be expelled isothermally at T_c without any enhancement of the void. Since the enhancement properties are systematic and independent of cooling rates, it does not seem reasonable to attribute this phenomenon to some metastable process associated with nucleation of the diamagnetic phase.

An additional aspect of the enhancement phenomenon is also consistent with the assumption that the hollow cylinder with a field in the void is an equilibrium configuration. In this explanation a hollow cylinder with a field in the void when $H_{\text{external}} = 0$ is a solution isolated from a source of excess solute. Consider an isolated solu-

Figure 56. Spontaneous increases of the field in the void of a thin-walled Sn hollow cylinder when cooled from above T_c in static fields. Data show the effect for two final temperatures.

Figure 57. Spontaneous increases of the field in the void of a thin-walled Pb hollow cylinder when cooled from above T_c in static fields. Data show the effect for three final temperatures.

Figure 58. Spontaneous increases of the field in the void of a thick-walled Pb hollow cylinder when cooled from above T_c to 4.2° K in various external fields.

Figure 59. Reversible changes with temperature of field (a) in the void of a Pb hollow cylinder in a constant applied field, and (b) in the void and the wall of a Sn hollow cylinder in the absence of an external field. Initial state was formed by cooling from above T_c to 2°K in an external field of 200 Oe. The external field was removed when the sample first reached 2°K .

tion in which one component exists both in the condensed phase and in the vapor phase. If such a system is subjected to temperature cycling, the component common to the vapor and condensed phases will exchange reversibly between both phases. The equivalent experimental test can be applied to a type I hollow cylinder by removing the applied field after the system has been cooled below the transition temperature for that applied field. It was found in such experiments that after cooling from T_c in the applied fields the changes are reversible with temperature and exhibit the

behavior shown in Figure 59(a). For a cylinder of given o.d. and i.d., the field in the void begins to exceed the value of the applied field at the temperature corresponding to the critical temperature for the applied field. As the temperature is lowered progressively, the field in the void increases with the same temperature dependence as that of the critical field of the wall material. At some temperature determined by the radial dimensions of the cylinder the enhancement ceases. Upon further cooling the field in the void remains constant. The changes occurring when the temperature is subsequently increased follow the same curves as those obtained during cooling.

When the external field is removed at a temperature below the transition temperature for the applied field, enhancement also occurs. The effect shows that the field lines pumped into the void come from field retained by the wall in the superconducting state. Moreover, subsequent temperature cycling between the temperature at which the external field was removed and lower temperatures shows reversible increases and decreases of the field in the void in the absence of an external field [Figure 59(b)]. The data shown were obtained by heating and cooling a Sn cylinder for 10 cycles between 2° and 1°K in the absence of an applied field after initial cooling from above T_c to 2°K in an external field of 200 Oe. The same reversible effect was observed in a 2-in.-long In cylinder (o.d., 760 mils; i.d., 150 mils) which was cycled between 2.0° and 1°K for 15 cycles. The In cylinder was cooled from 4.2°K in a field of 160 Oe. At 2°K ($H_c \cong 175$ Oe) the external field was removed. Subsequent cooling and heating between 2° and 1°K showed spontaneous reversible increases and decreases of the field in the void. Confirmation that field in the void was always equal to the critical field was obtained from subsequent isothermal magnetization measurements between 2° and 1°K . The results show that the wall acts as a reversible reservoir for field lines entering and leaving the void, i.e., no field leaves the system.

In a conventional solution the vapor component will attempt to establish a second equilibrium configuration because of the presence of a gravitational field. Since the vapor has mass, this second equilibrium requires a gradient in concentration with height. Eventually the component common to the vapor and condensed phases will leak out of the solution in an open system. Although the superconducting hollow cylinder is open at each

end, there is no second equilibrium involved associated with the property of mass which acts as a driving force to cause the retained fields to leak out.

D. SCHWEITZER, L. NICOLISI

SUPERCONDUCTIVITY AT LOW TEMPERATURES

Studies of superconductive phenomena at temperatures below 0.1°K have been initiated. Superconductivity of the graphite-alkali metal systems, many of whose normal-state electrical properties have been studied in this department, is being investigated. The interaction of low T_c superconductors and normal metals in layered structures (proximity effect) will be studied. The interesting feature of such systems is the long coherence lengths that are characteristic at low temperatures. Other problems to be studied include superconductivity in semiconductors and thermal excitations of vortices in type II superconductors. M. GARBER,

F. SALZANO, W. KIRK

SUPERCONDUCTIVITY OF THIN FILMS

The aims of the thin-film program are (1) to establish the ultimate limits of the transition temperature (T_c) in films, (2) to determine the maximum fields obtainable in superconductors, and (3) to answer the question of whether most of the two-dimensional systems obtainable in nature can be superconducting.

Figure 60. Sn and SiO layers. Alternating Sn and SiO layers are deposited as shown in insert. Approx. thickness ($\text{\AA}$): Sn 1, 160; SiO 1, 70; Sn 2, 40; SiO 2, 100; Sn 3, 200; SiO 3, 100; Sn 4, 85. Measuring current, $3.3 \mu\text{A}$; film size, $4 \times 2 \text{ mm}$.

Critical Temperature Measurements

It has been found that superconductor dielectric combinations can lead to high temperatures in pure metal layers. T_c 's have been obtained near 5.6°K in Al, 6.5°K in Sn, and about 4.6°K in In. All these temperatures are much higher than the bulk values. A theory of superconductor-dielectric-superconductor layers proposed by Douglass and Cohen appears to explain many of the effects found in the thin-film results. This theory predicts ultimate T_c 's near 40°K for certain superconductors, and so it is of great interest to determine whether this mechanism is operative and whether the theoretical structures that produce this high T_c can be made. The initial experiments done on layered structures show the large temperature rises previously mentioned. However, it is by no means clear that this is the only mechanism that can account for the high T_c 's. Some of the data on Sn-SiO-Sn layers are shown in Figure 60.

M. STRONGIN, O. KAMMERER,
J. CROW, P. DOUGLASS *

Ultrathin Films

By depositing metals on SiO layers previously deposited at low temperatures, it has been possible to make films with an average thickness of $<15 \text{ \AA}$. In all the materials thus far investigated, which

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Figure 61. Depression in T_c vs reciprocal resistance for Pb films deposited on previously deposited SiO layer.

include Al, Sn, Bi, and Pb, T_c decreases in the very thinnest films. Detailed measurements of T_c vs film thickness in Pb films are in agreement with a theory of Marčelja and Parks that considers phase fluctuations in the Ginzburg-Landau order parameter. These results are very pertinent to the question of long-range order in two-dimensional systems and essentially show that unless long mean-free path monolayers or other structures can be made, any increases in T_c due to quantization effects are improbable. Data on thin lead films are given in Figure 61.

O. KAMMERER,
M. STRONGIN, S. MARČELJA,* R. PARKS*

Critical Field Measurements

In order to continue investigating in some detail the upper critical field in very thin films on all materials, construction is nearing completion of a system in which ultrathin films can be prepared on cryogenic substrates and then measured *in situ*. The equipment allows the film to be rotated, after preparation, so that it can be measured in a field of about 115,000 Oe in the film plane. These measurements will help determine the highest critical fields obtainable in superconductors.

M. STRONGIN, J. CROW, O. KAMMERER

Proximity Effects Between Superconducting and Magnetic Layers

Precise measurements on the decrease in T_c of Pb films with overlays of iron have been made. Initial results show that most of the depression in the T_c of the Pb occurs with Fe layers of $< \frac{1}{2}$ monolayer in average thickness. Hence, only the Fe at the boundary appears to be effective in reducing T_c . Detailed measurements have also been made of the change in the T_c of the composite system with thickness of Pb. By measuring the films *in situ*, precise data have been obtained and compared with the general theory of the decrease in T_c due to the pair-breaking mechanisms.

J. CROW, M. STRONGIN, O. KAMMERER

Knight-Shift Measurements in Small Particles

Measurements are under way to determine the Knight shift in small particles in both the superconducting and normal states. These experiments are intended to determine the effect of quantization conditions on the normal-state magnetic properties, as well as the way in which pairing is

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Figure 62. AGS conductor cross section, showing detail of brazed joint.

modified in the superconducting state. It is also of interest to determine whether spin-flip scattering mechanisms such as spin-orbit scattering are operative in disordered low Z materials such as Al.

H. FINE, M. LIPSICAS,
M. STRONGIN, O. KAMMERER

High-Field Magnetoresistance in Bismuth

Longitudinal magnetoresistance measurements on Bi in longitudinal magnetic fields, up to 115,000 Oe, have been started. These measurements are preliminary to measurements on Bi films. In the case of films the effect of size quantization on various galvanomagnetic properties will be studied.

N. GARCIA, A. PASKIN, Y. KAO, M. STRONGIN

Metallography

Work in metallography during 1967 consisted primarily of routine examination of samples described elsewhere in this report. Examples of more than routine interest are described below.

AGS MAGNET COIL FAILURE

Water leakage was found in a series of brazed joints in the AGS main magnet coil conductors after $\approx 50 \times 10^6$ pulses. Brazing had been performed with use of a 72% Ag-18% Cu brazing alloy that melted and flowed at 1435°F. Figure 62 shows the design of the section, which incorporated an internal Cu brazing ferrule to strengthen the joint. Portions of failed and good sections of the Cu coils were examined in the Metallography Section. Special handling precautions had to be taken during sample preparation because the Cu was radioactive.

It appeared that failure had occurred on one side of the brazed joint. The joint was sectioned

Figure 63. Failed brazed joint. 4X.

perpendicular to the crack to provide a surface which revealed both the region of failure and the remainder of the brazed joint. Figures 63 and 64 show this cross section. The crack can be clearly seen at the top of the photomicrograph. In addition, a series of voids can be seen along the interface between the braze and base materials. The region of vertical structure appeared to be in the as-rolled condition, which indicated that the heat applied to that portion of the joint had been insufficient to melt the brazing alloy. Cracking was also found which propagated from the original region of failure into the internal areas of the joint. The condition of the brazed joints in these coils indicates the need for a new design and a change in the brazing procedure.

J. SADOFSKY,
A. CENDROWSKI

ULTRASONIC FATIGUE SPECIMENS

Two failed ultrasonic fatigue specimens were received from the Pulsed Reactor Development Group; they consisted of 60 vol % UO_2 -Mo cermet clad with Mo. Figure 65 shows the halves of a typical specimen and indicates that failure occurred toward the end of each machined section. Each specimen was sectioned, ground, and polished on a diamond-impregnated lap to insure maximum flatness and edge retention. Figure 66

Figure 64. Brazing joint. 250X.

represents a macro section of half of specimen No. 1 and shows the density of UO_2 spheres in the Mo matrix and the uniformity of the Mo clad. Figure 67 shows the microstructure of the clad and matrix material and the varied shape and distribution of a few UO_2 particles. Both samples exhibited excellent clad characteristics, with no visible voids in the bond. The clad on each section was measured to be 0.005 in., while the over-all section was 0.135 in. thick. This corresponds to the pretest condition of the specimens.

Figure 68 is a photomicrograph of the area adjacent to the failure. Microcracks are evident at the region of failure and in the Mo surrounding some of the UO_2 spheres in the same area. No cracking was noted elsewhere in either the clad or core. Failure probably was initiated in the core rather than the clad; the broken clad appeared to have failed in tension.

Failure occurred in both specimens through regions of high UO_2 density. It is thought that both better distribution and more uniform particle size would have added to the life of the specimens.

O. KAMMERER, J. SADOFSKY

Figure 65. Fatigue specimen failure in UO_2 -Mo cermet

Figure 66. Macro section of half of specimen No. 1. $2\times$.

Figure 67. Cermet-Mo interface. $250\times$.

Figure 68. Edge of fracture. $500\times$.

Figure 69. Schematic view of laminated composite conductor. Central member, Nb/Nb₃Sn conductor; outer members, Cu and stainless steel.

Figure 70. Photomicrograph of layers formed during Sn-Nb diffusion process. 500×.

ELECTRON PROBE EXAMINATION OF NIOBIUM-TIN TAPE

As part of the investigation into potential magnet materials for the AGS, laminated conductors were fabricated with a central core of Nb₃Sn. Of the vast number of superconducting materials known, the intermetallic compound Nb₃Sn has the highest combined critical current density, critical field, and critical temperature.

A flexible laminated conductor was formed by heat-treating a thin tape of Sn-coated Nb to produce a Sn-coated diffusion layer of Nb₃Sn surrounding a Nb core, and then laminating this tape between Cu tapes or Cu-stainless steel tapes by a soldering process to produce a laminated conductor. The normal approach to the production of this conductor is shown in Figure 69.

A specimen supposedly produced in the above manner was submitted for metallographic examination and electron probe microanalysis. Figure 70 shows the resulting photomicrograph after the specimen was sectioned and polished. Electron probe analysis using a beam collimated to 2 μ identified all the various layers. This analysis, shown in Figure 70, indicates that three Pb-Sn solder strips were used instead of the expected two, and thus there were four Nb₃Sn layers.

J. SADOFSKY

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Heat Transfer Studies

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The program of the Heat Transfer Group continued to be concerned primarily with liquid-metal heat transfer. The objective was to gain greater understanding of the fundamental mechanisms of liquid-metal heat transfer and to obtain reliable data and develop correlations for use in the thermal design of (a) central power plants of the liquid-metal-cooled fast-breeder type, and (b) auxiliary, special-purpose power plants of the alkali-metal Rankine-cycle type. Problems in both single-phase (liquid) heat transfer and two-phase (vapor-liquid) heat transfer were investigated. Both analytical and experimental studies were pursued. In addition to this work, a small effort was directed toward heat transfer problems in the area of high-temperature, direct-conversion systems, e.g., magnetohydrodynamic (MHD) systems. A survey was made of the current status of knowledge, and some analytical studies were pursued. The Heat Transfer Research Group also continued publication of the *High-Temperature Liquid-Metal Technology Review*.

Some results from various projects are summarized below.

BOILING LIQUID METAL STUDIES

In the past year interest was centered on the phenomenon of incipient-boiling superheat in alkali metals. The specific objective of the study was to determine the effect of operating history (of a heater surface/liquid metal combination) on the magnitude of superheating required to initiate boiling. Such information is directly relevant to the design and operation of liquid-metal-cooled fast reactors.

The analytical part of the study was directed toward development of a phenomenological model for the conditions (a) prior to boiling and (b) at boiling incipience. It was first argued that Hsu's

theory [*J. Heat Transfer* **84**, 207-16 (1962)], which is commonly used to estimate incipient boiling superheats for ordinary fluids, defines a necessary but insufficient criterion for incipient boiling of alkali metals. Because of their high thermal conductivities, it was postulated that the important criterion for liquid-metal systems is the degree of cavity deactivation (prior to boiling) rather than the limiting thickness of the thermal boundary layer. Extending some concepts introduced by Holtz (ANL-7184, 1966) resulted in the following expressions for predicting incipient-boiling superheats for alkali metals:

$$P_v - P = \frac{\sigma(P' - P_v')}{\sigma \cos \theta} - \frac{G_o}{r_d^3} \\ \times \left[\frac{T}{(1 + 2 \tan \theta)} + \frac{\sigma T'}{\sigma' F(\theta) \cdot \cos \theta} \right], \\ F(\theta) = 1 - (\tan \theta)(1/\cos \theta)^3(1 - \sin \theta)^2(2 + \sin \theta), \\ r_d = \text{real root of the equation,} \\ r_d^3 - \left(\frac{2\sigma' \cos \theta}{P' - P_v'} \right) r_d^2 - \frac{G_o T'}{(P' - P_v') F(\theta)} = 0, \\ \Delta T_s = \text{superheat} = T - T_s,$$

where

- T = superheat temperature = saturation temperature at vapor pressure P_v ,
- T_s = saturation temperature at system pressure P ,
- P = system pressure at boiling incipience,
- P_v = vapor pressure corresponding to superheat at boiling incipience,
- P' = system pressure under preboiling deactivation condition,
- T' = system temperature under preboiling deactivation condition,
- P_v' = vapor pressure corresponding to T' ,
- σ, σ' = surface tension at T, T' , respectively,
- θ = one-half of cavity apex angle, and
- G_o = empirical constant, measuring amount of inert gas trapped in a cavity at time of initial fill.

For surfaces of standard commercial finishes, with a range of cavity shapes and sizes, θ should be taken to approach zero in order to obtain the minimum superheat required to initiate boiling.

Experimental data were obtained in a high-temperature, forced-convection loop for comparison with the above theory. Potassium was used as the test fluid, but the general results and their comparisons with the model should be similar for any alkali metal. Starting with a new test section (tubular boiler), the system was filled under vacuum, deoxidized for a set period, then subjected to deactivations with the potassium at various pressures, temperatures, and subcoolings. After each of these deactivation periods, the superheat required for incipient boiling was measured. The ranges of conditions, during deactivation and boiling incipience, were as follows:

	Deactivation	Boiling incipience
Pressure, psia	5-40	8-24
Potassium temperature, °F	900-1508	1295-1600
Liquid subcooling, °F	10-380	-
Surface heat flux, Btu/(hr · ft ²)	-	2000-50,000
Liquid velocity, ft/sec	0.2	0.2

Figure 1. Incipient boiling superheats after deactivation at 1180°F.

Some results are presented in Figures 1 and 2. Figure 1 shows incipient boiling superheats at $P = 16$ psia after deactivation at $T' = 1180^\circ\text{F}$. The independent variable in this family of data points was the deactivation pressure, P' . The measured superheats increased with increasing P' , from 17°F at $P' = 5$ psia to 114°F at $P' = 25$ psia. The curve on the figure represents superheats calculated from the proposed theory. The trend of the data appears to be in agreement with the theory. The calculated curve is seen to pass through the data points with a mean deviation of $\approx \pm 12^\circ\text{F}$. Figure 2 presents data obtained for incipient boiling at various pressures (P) after deactivation at $P' = 12$ psia and $T' = 1166^\circ\text{F}$ (200°F subcooling). Again, the curve calculated by the proposed model is seen to be in good agreement with experimental results.

EFFECTS OF SOLID-LIQUID INTERFACE CHARACTERISTICS ON HEAT TRANSFER WITH SODIUM

This project was started in order to study the effects of heat transfer surfaces on the heat transfer

Figure 2. Incipient boiling superheats at various pressures.

behavior of sodium. For this, a new figure-eight loop has been designed; it will incorporate an existing NaK loop as the cold portion. The reference heating-surface material is stainless steel, and the following information will be obtained (on a single test section): (a) liquid-phase heat transfer coefficient as a function of flow rate, particularly at the lower Peclet numbers, (b) wall superheats ($t_w - t_{sat}$) for incipient boiling under conditions of natural convection as a function of pressure and heat flux, (c) natural-circulation-boiling heat transfer coefficients as a function of pressure and heat flux, and (d) wall superheats ($t_w - t_{sat}$) for incipient boiling under conditions of forced convection as a function of pressure, heat flux, and flow rate. The last item, considered the most important, has direct relevance to the safety aspects of sodium-cooled nuclear reactors. Independent test parameters include (a) inert gas content of sodium, (b) oxygen content of sodium, (c) microstructure of heating surface, and (d) temperature-pressure history of sodium-surface combination. Data will be taken at temperatures up to 1600°F, at Peclet numbers in the range 20 to 1000, and at pressures in the range 1 to 15 psia.

The test section will be a vertical, annular-shaped channel, with the heat transferred from the inner wall. High-flux electrically heated rods will be used initially, and the test section is designed to permit rapid replacement. The loop and components have been designed and fabrication has been started. The facility is scheduled to be completed by the end of calendar year 1968.

HEAT TRANSFER TO MERCURY FLOWING IN-LINE THROUGH ASYMMETRIC ROD BUNDLES

Analytical studies carried out a few years ago at Brookhaven showed that eccentricity can cause a large reduction in the average heat transfer coefficient for flow of liquid metals through annuli. Asymmetry in rod bundles should show similar effects.

During the past year an experimental project was carried out to measure the effect of varying displacements of the central rod in a bundle consisting of thirteen 1/2-in.-o.d. rods. The rods are arrayed in an equilateral, triangular pattern with a pitch:diameter ratio of 1.75. The bundle has three test rods – the central one and two others adjacent to it. The two adjacent rods can be placed in any two of the six adjacent locations (see Figure

3). Each of the test rods has nine thermocouples evenly distributed around its circumference at an axial position in the bundle where the temperature and velocity profiles are fully developed. These thermocouples are imbedded slightly below the surface. The test rods are special high-flux electrical heaters. Three different types of sheath materials are being tested – copper, stainless steel, and nickel. All rods in the bundle are uniformly heated.

So far, results have been obtained on the copper- and stainless steel-sheathed rods. Some typical results obtained with the former are shown in Figures 3 to 7. As the central rod *B* is moved toward rod *C*, the average heat transfer coefficients for rods *A*, *B*, and *C* decrease, and the circumferential variation of the wall temperature for each of these rods increases. Rod *C* shows these effects more than either rods *A* or *B*, as one would predict, because it is the most confined. Figure 3 shows the results obtained on rod *C*. When rod *B* was moved 53% of the maximum distance toward rod *C*, the average coefficient for rod *C* dropped $\approx 18\%$; when it was moved 80%, the coefficient dropped $\approx 35\%$.

Figures 4 and 5 show the corresponding information for rods *B* and *A*. As one would expect, the effect of moving rod *B* toward rod *C* upon the heat transfer characteristics of rod *A* is relatively small.

While the average Nusselt number for each of rods *A*, *B*, and *C* drops, as rod *B* is moved toward rod *C*, those of rods *D* and *E* rise, but the extents of the increases are appreciably less than those of the decreases. The conclusion is that whenever a rod moves off-center the heat transfer capability of the bundle drops. Figure 6 shows the relative drop in the heat transfer coefficient of rod *B* as it is moved toward rod *C* and as it is moved toward a point midway between rods *A* and *C* for both the copper and stainless steel sheaths. The stainless steel sheaths permit much less circumferential heat flow, which means that the heat must transfer over a greater distance in the flowing mercury coolant. This then results in a lower average heat transfer coefficient.

Figure 7 shows the effect of moving rod *B* (toward rod *C*) on the circumferential variation of the surface temperature of rod *B* for the copper sheath.

Definitions of terms used in the figures are as follows:

Figure 3. Heat transfer characteristics of rod C, showing the effect of moving rod B toward rod C, for mercury flowing in-line through an unbaffled rod bundle. Rod B is the central rod in a 13-rod bundle.

Figure 4. Heat transfer characteristics of rod B, showing the effect of moving it toward rod C, for mercury flowing in-line through an unbaffled rod bundle. Rod B is the central rod in a 13-rod bundle.

Figure 5. Heat transfer characteristics of rod A, showing the effect of moving rod B toward rod C, for mercury flowing in-line through an unbaffled rod bundle. Rod B is the central rod in a 13-rod bundle.

Figure 6. Heat transfer to fully developed turbulent in-line flow of mercury through an unbaffled rod bundle. Experimental results showing the effect of rod B displacement on its average heat transfer coefficient.

Average Nusselt number = Nu

= hD_e/k , dimensionless,

Peclet number

= $Pe = D_e v_a \rho C_p / k$, dimensionless,

$\bar{h}$ = circumferential average heat transfer coefficient,

$\bar{h}_{asym}$ = circumferential average heat transfer coefficient for asymmetrical situation,

h_{sym} = heat transfer coefficient for symmetrical situation,

D_e = equivalent diameter,

k = thermal conductivity,

v_a = average linear velocity of coolant,

ρ = density of coolant,

C_p = specific heat of coolant,

y = distance between heaters B and C,

t_w = local surface temperature of rod,

t_b = bulk temperature of coolant,

$\bar{q}$ = average surface heat flux,

$t = t_w - t_b$, and

ζ = ratio of actual rod displacement to maximum possible displacement.

ANALYTICAL STUDIES OF ENTRANCE REGION HEAT TRANSFER

In this report period two problems of entrance-region heat transfer were investigated analytically. In both cases exact solutions for the temperature distribution were obtained.

The first problem was that of laminar flow in tubes with axial conduction and heat loss at the

Figure 7. Circumferential variation of surface temperature of rod *B*, showing the effect of moving it toward rod *C*. See Figure 5 for spatial arrangement of rods.

wall. The temperature solution was obtained in series form, wherein the eigenvalues, eigenfunctions, and expansion coefficients were functions of the Peclet number (N_{Pe}) and a heat loss parameter (Δ) defined as

$$N_{Pe} = \frac{D\bar{u}\rho C_p}{k},$$

$$\Delta = \frac{hD}{2k},$$

where

- D = tube diameter,
- $\bar{u}$ = average velocity,
- h = transfer coefficient for wall heat loss,
- ρ = fluid density,
- C_p = fluid heat capacity, and
- k = fluid thermal conductivity.

Determination of the first twelve eigenvalues, eigenfunctions, and the series expansion coefficients was made for Peclet numbers of 1, 5, 10, 20,

30, 50, 100 and infinity, and for the radiation parameter, Δ , of 2, 10, and 100. Examination of the thermal-entry-region temperature profiles revealed that the effect of axial conduction tends to raise the wall temperature while lowering the fluid temperature near the central region of the channel. As a result, the local Nusselt number at a fixed value of $x/r_o N_{Pe}$ increases. In general, such an effect was found to be negligible if the Peclet number exceeds 50. It becomes increasingly significant, however, as the Peclet number is lowered.

The second problem was that of entrance-region heat transfer in MHD channel flow with Joule heating and allowing for axial conduction and viscous dissipation. Hartmann flow was assumed for the velocity distribution. Temperature solutions corresponding to a few electric field magnitude factors, e , of practical importance and arbitrary values of the heat generation parameter, κ , were obtained. Figure 8 illustrates the variation of local temperature profiles for a Hartmann number of

Figure 8. Local temperature profiles with and without axial conduction for $M=10$, $N_{Pe}=10$, and $\epsilon=0.8$.

10 and $\epsilon=0.8$. (In the figure, $\gamma=y/a$, $\theta=(T-T_0)/(q_w a/k)$, a =one-half the channel height, and q_w =heat flux at wall.) It was found that, if $\kappa=0$, increasing the Hartmann number tends to cause an increase in local Nusselt number. This trend was found to be reversed, however, for κ values different from zero. The Nusselt number appears to be quite sensitive to the variation of κ if the Hartmann number is relatively large. For fixed Peclet number and κ , increasing the electric field magnitude factor causes diminution in the local Nusselt number. The effect of axial conduction was found to be relatively unimportant if the Peclet number exceeds ≈ 100 . For smaller Peclet numbers, however, such an effect becomes quite appreciable.

ANALYTICAL STUDY OF THE THERMODYNAMICS OF EVAPORATING ENTRAINED LIQUID DROPLETS

There is very little experimental or theoretical information available on the behavior of evaporating droplets in two-phase flow. The problem is important because in some regimes of two-phase flow entrained droplets represent a major fraction of the liquid flow, and the rate of droplet vaporiza-

tion could be an important factor in over-all heat transfer. The objective of this project was to formulate some quantitative relationships for estimating rate of evaporation and the transient temperatures of droplets entrained in vapor.

The method of approach was to first analyze the behavior of a single droplet, initially at a uniform temperature and saturation pressure, when it is suddenly injected into a volume of vapor at a lower pressure. The driving force for evaporation is the time-dependent vapor-pressure difference. The governing heat and mass transfer equations were derived and solved numerically for a number of sample cases of potassium droplets in potassium vapor. The solutions give the transient temperature of the droplet, the droplet radius, and the vapor temperature profile in the vicinity of the droplet. Results were obtained for both cases of saturated vapor and cases of superheated vapor. The results show that the evaporation process consists of two distinct time domains: one during which the evaporation rate is governed primarily by transient, nonequilibrium, vapor pressure difference; and the second during which the droplet is essentially at equilibrium pressure and further evaporation is governed by vapor-phase heat transfer.

The next step in the analysis is to predict the vaporization behavior of an entrained droplet in two-phase flow situations where local pressure decreases in the flow direction. Using the Lagrangian approach, an attempt will be made to determine the time scale and dimensional scale of the zone-of-influence of the evaporating droplet. This will then indicate the degree to which entrained droplets can affect the over-all two-phase flow conditions.

ANALYTICAL STUDY OF TRANSIENT HEAT TRANSFER IN MAGNETOHYDRODYNAMIC CHANNEL FLOW

The objective of this study was to determine the effects of step changes in pressure gradient, magnetic field, and wall temperature on heat transfer in MHD duct flow. The energy equation for this problem is independent of the momentum and Maxwell equations and was derived to be

$$\begin{aligned} N_{Pr} \frac{\partial \theta}{\partial t} + V N_{Pr} \frac{\partial \theta}{\partial x} \\ = \frac{1}{N_{Re}} \frac{\partial^2 \theta}{\partial Y^2} + \frac{A^2}{N_{Rm}} \left(\frac{\partial b}{\partial Y} \right)^2 + \frac{1}{N_{Re}} \left(\frac{\partial V}{\partial Y} \right)^2, \end{aligned}$$

where

- N_{Pr} = Prandtl number,
- N_{Re} = Reynolds number,
- N_{Rm} = magnetic Prandtl number,
- b = induced magnetic field,
- V = fluid velocity,
- θ = temperature,
- t = time,
- x = axial distance variable,
- Y = transverse distance variable, and
- A = a function of Hartmann number.

A solution of the energy equation for fully developed flow was found in the form

$$\theta = 2 \sum_{k=1}^{\infty} \left\{ \theta_{ki} \exp\left(-\frac{\alpha_k^2 t}{N_{Re} N_{Pr}}\right) + \frac{1}{N_{Pr}} \int_0^{\tau} \exp\left[-\left(\frac{\alpha_k^2}{N_{Re} N_{Pr}}\right)(\tau - \gamma)\right] \times \left[\frac{A^2}{N_{Rm}} h_1(k, \gamma) + \frac{h_2}{N_{Re}}(k, \gamma) \right] d\gamma \right\} \cos(\alpha_k) Y,$$

where $\alpha_k = [(2k-1)\pi]/2$, $h_1(k, \gamma)$ and $h_2(k, \gamma)$ are each double infinite series, and θ_{ki} is the Fourier transform of the initial temperature distribution.

Temperature profiles and Nusselt numbers were obtained from this solution. Figures 9 and 10 illustrate the effects of a step increase of N_{Re} on average temperature and Nusselt number, respectively. Physically, this corresponds to increasing N_{Re} by increasing the pressure gradient in the presence of a uniform magnetic field. The temperature is seen to increase continuously with time to a steady-state value, while N_{Nu} increases to a maximum and then decreases. Initially, the wall heat flux increases faster than the temperature difference, which explains the rising part of the curve. Eventually, the rate of rise of θ_{av} overtakes the wall heat flux which results in a maximum N_{Nu} after which it decreases continuously to a steady-state value.

Waste Disposal Studies

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As part of the AEC program for the conversion of high-level radioactive waste solutions to stable solids, a process has been developed at Brookhaven for incorporating fission products into phosphate

Figure 9. Variation of mixed mean temperature with time following a step increase of Reynolds number.

Figure 10. Variation of Nusselt number with time following a step increase in Reynolds number.

glass. The phosphate glass process is one of three waste solidification processes selected for evaluation on a full-prototype scale in a demonstration program at Battelle Northwest Laboratories (BNWL).

In the Brookhaven process phosphoric acid is mixed with the high nitric acid content Purex waste and the resultant solution is heated to 130° to 150°C in a specially designed evaporator to drive off water and most of the nitric acid. The concentrated product is then converted to a glass by heating to 1200°C in a platinum crucible. Development of the process for continuous operation, as facilitated by maintaining an all-liquid system, has been a major factor in the program.

Pilot plant studies at Brookhaven over the past four years have provided basic information for the design of the demonstration plant which will be operated with high-level wastes in the BNWL fuel recycle hot cell.

PILOT PLANT

Operation of the pilot plant over the past year has centered on problems encountered in processing a number of new Purex wastes reflecting higher fuel burnup and more advanced fuel reprocessing techniques. Initial operation of the BNWL prototype will be with Purex-1 and -2, the compositions of which are given in Table 1. A number of pilot plant runs were made with these waste compositions and the results are shown in Table 2. In preparing the feed solutions for these runs, considerable variation was made in the phosphoric acid and sodium concentrations, the effect of which was of primary importance in determining the upper limit of temperature for the evaporator operation. With Purex-2, which contains sulfuric acid resulting from the use of ferrous sulfamate in the fuel reprocessing, plant operation was entirely satisfactory and without incident. With Purex-1, which does not contain sulfuric acid, satisfactory operation was more difficult to attain particularly in the case of the evaporator and with respect to maintaining smooth flow in the pipe between the evaporator and the melter. With additional laboratory studies carried out in support of the pilot-plant operation, it was found that the manganese, which had been included in the waste formulation as a substitute for ruthenium, was a chief offender in promoting plugging of the lines. The elimination of manganese, which is not a normal constituent of

Table 1
Purex Wastes for WSEP Demonstration

	Purex Waste-1	Purex Waste-2
H ⁺	5.00 M	5.00 M
Fe ⁺³	0.93	0.445
Cr ⁺³	0.012	0.024
Ni ⁺²	0.005	0.010
Al ⁺³	0.001	0.001
Na ⁺	0.138	0.930
U ⁺⁶	0.010	0.010
Hg ⁺²	<0.001	<0.001
NO ₃ ⁻ -NO ₂ ⁻	8.80	6.44
SO ₄ ⁻²	-	0.870
PO ₄ ⁻³	0.003	0.006
S ₂ O ₃ ⁻²	0.010	0.010
F ⁻	<0.001	<0.001
F.P.'s ⁽³⁾ as M ⁺²	0.477	0.477
M ₂ O	1.99	1.68
Volume	100 gal/tonne (378.5 liter/tonne)	100 gal/tonne (378.5 liter/tonne)
Heat at 1 yr	12.2 W/liter	12.2 W/liter
6 yr	2 W/liter	2 W/liter
Activity at 1 yr	2200 Ci/liter	2200 Ci/liter
6 yr	710 Ci/liter	710 Ci/liter

Table 2
Results of Corrosion Study (in./yr)

Metal	40% H ₂ SO ₄ at 120°C	60% H ₂ SO ₄ at 142°C	85% H ₂ SO ₄ at 150°C	85% H ₂ SO ₄ at 220°C
Pb	0.0055	0.0615	-	2.675
Irium 98	-	-	0.371	-
Irium G	-	-	0.715	-
Pt	-	-	0.00008	0.00005
Ta	-	-	0.00018	0.0020
Au	-	-	0	0.00004

Purex waste, and the addition of iron as a substitute for ruthenium resulted in considerable improvement in plant operation with Purex-1 and no further problems have been encountered to date with respect to plugging of lines. In the course of this work a number of design changes were made in the pilot plant, particularly with respect to the specific gravity and weight-factor tubes, resulting in the elimination of plugging which had occurred periodically in these areas with Purex-1 feed.

The original evaporator for the Brookhaven pilot plant was constructed of stainless steel. During the past year, after 49 runs, a slow leak devel-

Figure 11. Decontamination factor vs distillation pressure of Purex-2 melter off-gas condensate.

oped in the tube bundle that necessitated a complete shutdown and disassembly of the unit. Examination revealed considerable corrosion of the 304 SS fins and draft tubes. Bolts and fittings made of 316 SS were badly attacked especially in the area where the material was subject to work hardening. Also, the welds and adjacent areas showed definite signs of corrosion. Stagnant fluid regions where Teflon caps had been used to cover 316 SS fittings were severely attacked. Most of the corrosion seemed to have occurred during the more recent processing of Purex-1 waste, with a total operating time of 3600 hr, since only moderate corrosion was evident when the vessel was examined 6 months earlier after an ≈ 8000 -hr exposure to Purex-2 solution. In the course of operations with Purex-1, the concentration of H_3PO_4 was varied from test to test, and it was apparent on the basis of subsequent corrosion tests with 304, 304L, 316, and 316L SS and titanium that the greater part of the corrosion occurred when H_3PO_4 was present in larger concentrations. After consideration of the relative costs of using stainless steel and the more corrosion resistant titanium, as well as the additional length of time the evaporator is

Figure 12. Fractionator for continuous separation of HNO_3 , H_2SO_4 , and H_3PO_4 . Designed for increased retention of fission products (including Ru) with the H_3PO_4 still bottoms.

expected to be in service, the new tube bundle and inner evaporator shell were fabricated of 347 SS.

MELTER OFF-GAS TREATMENT

Experiments during the past year have substantiated the prediction that the melter off-gas condensate can be separated into its major components, nitric acid, sulfuric acid, and phosphoric acid, by distillation with virtually all the Ru remaining with the phosphoric acid still bottoms. The basic principle of operation is that all the nitric acid can be removed from the still at relatively low temperature prior to volatilization of sulfuric acid. It was found that operating at temperatures associated with modest vacuum proved most suitable. In earlier work at Brookhaven with melter condensates spiked with Sr^{90} and Ce^{144} , it was apparent that decontamination factors of the order of 10^5 could be realized by a single distillation. These values also indicated that the contaminant was carried over by entrainment. During the past year several experiments were carried out with Ru^{102} as a tracer. Decontamination factors as high as 10^4 were achieved when the distillation pressures were in the neighborhood of 20 mm Hg.

Values for ruthenium decontamination factor vs stillpot pressure are shown in Figure 11. Distillation equipment, including an 8 × 18-in. tantalum stillpot to be used in conjunction with the operation of the pilot plant, is now being assembled. Tantalum was selected as the material of construction on the basis of results of corrosion tests as shown in Table 2.

In experiments thus far, only batch distillation techniques have been demonstrated, but the advantage of higher throughput with continuous processing has prompted a study of the latter method of operation. Figure 12 illustrates one continuous method of separating the melter condensate components in a fractionator of special design. As before, the distillation temperature would be kept low until the nitric acid was removed to assure that ruthenium would remain in the lower oxidation, or nonvolatile, state in the still bottoms. Once nitric acid was removed, the temperature would be raised to volatilize the sulfuric acid. As shown in the figure, *BC* is a controlled temperature section of such a length that all the nitric acid fed to the vessel at *A* would be volatilized and the sulfuric acid, phosphoric acid, and fission products would be collected as a liquid at point *C*. A condenser in the region above *A* would provide for some refluxing of nitric acid. The sulfate and phosphate liquid components would leave this section of the column at *C* and enter a second column section through a liquid trap at *D*. The two sections of the column would be separated from each other by a liquid trap but would be maintained at the same reduced pressure (say, 18 mm Hg). In the lower section, to be operated at a much higher temperature, sulfuric acid would be volatilized and removed at *E*, and the phosphate and the fission products, including ruthenium, would make up the still bottoms. An alternative method would be to carry out the distillation without the internal condenser in the lower section of the column, but with the use of vapor-phase filtration for further decontamination of the vapors by removal of entrained material.

STABILITY OF PLATINUM

The selection of platinum as the construction material for the high-temperature crucible has prompted extensive studies to determine the effects, on the strength of the metal, of high temperature, and the extent and effect of any migration

of waste components into the platinum. The overall study involved: (1) measurement of creep strength of virgin Englehard E-2G grade 99.95% platinum at 1250°C under stresses of 50 and 100 lb/in.² for 6000 hr; (2) measurement of creep strength of E-2G 99.95% platinum specimens cut from a crucible that had been used to process simulated Purex-2 waste containing a full complement of waste elements, at a temperature of 1260°C, a stress of 100 lb/in.², and over a period of 3000 hr; and (3) ion microprobe mass spectrograph analysis of specimens cut from the same crucible to determine the extent of waste element penetration.

The investigation was made with the cooperation and assistance of Englehard Industries who supplied assayed platinum, Battelle Memorial Institute who performed the creep tests, and the Geophysical Corporation of America (GCA) who made the mass spectrographic determinations under contract with Brookhaven.

The virgin platinum specimen stressed at 50 lb psi was elongated 0.69% in the first 1800 hr, and the specimen stressed at 100 psi was elongated 1.48% in the first 2000 hr. In both cases there was an apparent absence of secondary creep. The results of the creep measurements made with the specimens cut from the crucible showed a strain value of 0.3% in 2000 hr. Virtually all the elongation occurred in the first 400 hr and there was little indication that there would be any further creep.

The ion microprobe studies revealed no evidence of massive penetration of the waste elements into the platinum during the glass-forming process. Ruthenium, rhodium, and palladium penetrated to a greater extent than the other waste elements. The rhodium and palladium intensities as shown in the spectrographs fell off relatively rapidly in the platinum sample exposed to the vapor phase but more slowly in the other two. The lower concentration of the metals in the vapor-phase sample indicated less transport through the vapor. The reverse is true for ruthenium which showed high penetration in the vapor-phase sample, as would be expected if ruthenium tetraoxide were present.

The results of creep measurements with the exposed platinum specimen showed that the strain value was 0.3% as compared to 1.48% for the virgin platinum. This suggests an increase in strength due to slight penetration of these elements as would be expected, for example, in the case of rhodium.

FLUIDIZED-BED VOLATILITY WASTE DISPOSAL

The investigation was continued on the development of a process for the ultimate disposal of the high-level wastes generated in fuel reprocessing by means of fluidized-bed volatility. The process is based on dispersal of the bed material, i.e., aluminum oxide and fission products, in glass matrices to give a stable product suitable for initial transporting to a disposal site and long-term storage. Of the several glass types investigated, those of the soda-lime composition offered the best set of advantages through physical and chemical integrity and good thermal conductivity, together with low raw materials cost. The process is described in BNL 50023 (S-69).

During the past year particular emphasis has been placed on establishing design criteria for a proposed waste processing facility for the ORNL fluidized-bed volatility pilot plant. This involved the design, construction, and operation of a small-scale demonstration unit capable of handling a 6-in.-diam $\times$ 12-in.-long process vessel. Studies were carried out on glass-alumina bed mixing, container corrosion, fluoride retention, and the effects of time, temperature, and fluoride content on product quality.

In light of the space limitation in the ORNL process cell and the difficulty involved in transfer of the waste solids before the fusion step, the design was based on carrying out the mixing step in the final waste container. Experiments were carried out in a Plexiglas model of the waste can by using different colors of Al_2O_3 to trace the movement of different sizes and shapes of particles during mixing.

Two methods of mixing were first considered – fluidizing and tumbling. Best results were obtained with end-over-end tumbling, and good mixing was quickly achieved in this manner with a vessel having an L/D ratio of 10 and filled to 95% of capacity. Several glass-alumina charges mixed in this manner were subjected to normal processing conditions, and the products, in general, were homogeneous and comparable to previously made hand-mixed samples.

With respect to the selection of a construction material for the final waste container, corrosion tests were run on stainless steel, nickel, brass, copper, and mild steel. Small crucibles were made of the various metals and exposed to glass-bed mixtures of varying fluoride content for periods up to

100 hr at a temperature of 950°C, under conditions far more severe than those anticipated in practice. In general, stainless steel demonstrated superior corrosion resistance. Three types, 304, 316, and 347 SS, were further tested with the result that all three performed equally well.

A series of experiments was carried out in an effort to control formation of voids in the glass matrix by programmed heating during the fusing step. Because of the low thermal conductivity of the unfused bed-glass mixture, the gaseous products formed in the central region only after the outer region had become partially fused and were, therefore, somewhat impervious. The result was the formation of a sponge-like structure in the central region. A solution to the problem was found by subjecting the material to a preheat treatment before fusing to permit the formation and escape of volatiles before any part of the mixture reached fusion temperatures. In a series of experiments, performed to determine the feasibility of the programmed heating method, it was indicated that the preheat treatment definitely contributed to the control of formation of voids. Specifically, it was found upon sectioning that preheating at 500°C yielded a highly dense product that showed a smooth low-void structure.

Some effects of composition, furnace temperature, and firing time on samples cast in 1 $\frac{3}{8}$ -in.-diam $\times$ 4-in.-high and 4 $\frac{1}{8}$ -in.-diam $\times$ 4 $\frac{3}{8}$ -in.-high containers were determined. An increased fluoride content resulted in a decrease in bulk density and a decrease in shrinkage after firing. Firing temperatures of 850° and 900°C were required for fluoride-free and fluoride-containing samples, respectively, to produce a hard, nonabradable product. A 6-hr firing time was required for the larger castings as compared with a 1-hr firing time for the smaller ones. In general, the fluoride-containing specimens were free of large cavities that existed in the fluoride-free castings.

Program activities were suspended in August as a result of the decision to terminate activity on the ORNL fluid-bed volatility demonstration pilot plant.

KRYPTON AND XENON REMOVAL FROM OFF-GASES FROM FUEL REPROCESSING

A system is being developed for removing the Kr and Xe from gas mixtures such as those from nuclear fuel reprocessing. The objective is to select

the best combination from among the proposed steps which involve liquefaction, distillation to remove N_2 , fractionation to remove some O_2 , fluidized-bed reaction with H_2 for further removal of O_2 , and adsorption of Kr and Xe on solid adsorbents.

The process off-gases would initially be passed through scrubbers to remove acid constituents and water vapor. If H_2 were present, it would be removed by fluidized-bed reaction with O_2 .

First efforts are being directed toward the study of the adsorption of Kr and Xe on activated charcoal and molecular sieve materials. Since adsorption is indicated to be the final step in the over-all process, the objective in the initial phase of the study is to determine the degree of Kr-Xe concentration required in the distillation and O_2 -reaction steps for the adsorbents to operate under optimum conditions.

The first tests will be run on Kr alone. A stream of nitrogen containing 100 ppm Kr – the concentration in an average reprocessing off-gas stream – will be passed through columns containing various adsorbents, at selected temperatures down to -300°F . The gas will be traced with Kr^{85} and analyzed by counting techniques. The column exit streams will be monitored to determine the “break-through” point, when the adsorbent will be saturated with Kr under the test conditions.

A cryogenerator, capable of producing temperatures down to that of liquid air, will be used in conjunction with an air recirculator to feed a cold-atmosphere chamber. This will permit control at any point over the entire temperature range from ambient to -300°F , instead of limiting the system to certain specific levels attainable by the use of liquefied gases or dry ice. Temperatures will be measured by means of thermocouples brazed directly to the adsorption columns which are made of copper. Provision will also be made for testing at pressures above atmospheric.

The cryogenic unit has been installed and connected to the cold-atmosphere chamber and the whole complex is now under test.

The Kr^{85} counter-analyzer has been delivered but has not yet been tested in the system. It was, however, tested independently before delivery. The test gas mixture of nitrogen and 100 ppm Kr and tracer Kr^{85} is currently being made up; this is a necessary precursor to testing and calibrating the analyzer.

Four adsorption columns along with their heat economizer-exchangers have been built and in-

stalled in the cold chamber. The piping and flow-meter system is almost complete and is undergoing leak-testing along with the adsorbents.

Safety Studies

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The primary objective of this continuing program is to develop a fundamental understanding of the chemical reactions, mechanisms of release, and transport behavior of the fission products and radioactive aerosols emanating from nuclear materials under conditions likely to be encountered in reactor accidents. During the past year, studies related to the safety of sodium-cooled fast reactors received primary emphasis although some effort was also expended to complete work related to water-cooled reactors.

SODIUM STUDIES

An investigation of the behavior of fission products in sodium systems is under way to provide information on their volatility, distribution, and the rate and extent to which they would be released in the event of an accident. Studies are currently in progress to measure both thermodynamic and transport properties of sodium solutions containing Cs, Rb, Sr, NaI, Ba, Te, and Sb.

Measurements of the excess thermodynamic properties of infinitely dilute NaI solutions in sodium were completed. The partial molar excess free energy of mixing values, $\overline{\Delta F}^E$, divided by RT are plotted vs reciprocal absolute temperature, T , in Figure 13. Since

$$(\overline{\Delta F}^E/RT) = (\overline{\Delta H}/RT) - (\overline{\Delta S}^E/R),$$

the slope of this plot is equal to the heat of mixing, $\overline{\Delta H}$, divided by the gas law constant, R . The solid line shown in the figure gives a heat of mixing of 15.9 kcal/mole and excess entropy of mixing, $\overline{\Delta S}^E$, of 6.7 eu.

Values of these excess thermodynamic properties, determined experimentally and by several different analytical methods, are tabulated in Table 3 for comparison. The values tabulated in the first four rows were calculated from the Na-NaI phase diagram published by Bredig and Bronstein [*J. Phys. Chem.* **64**, 64 (1960)]. It is evident that the Borelius power series method yields

results that are far too low at infinite dilution. This is because only one term in the series contributes to the excess thermodynamic properties at this limiting concentration. The Henry's law approximation also leads to low values for this system. The one-parameter equation employed by Pitzer, however, gives results that are in reasonably good agreement with the experimental values.

A two-parameter equation was employed to calculate the excess properties from the phase diagram. Although more tedious to use, this equation leads to a closer approximation of the actual values, as seen by comparing the data given in the third, fourth, and fifth rows of Table 3.

Recently, the excess thermodynamic properties were calculated using Prigogine's (*The Molecular Theory of Solutions*, North-Holland Publ. Co., 1957) average potential model for liquid solutions based on statistical mechanical considerations. A Lennard-Jones 6-12 potential was found to adequately represent the interactions in solution, suggesting that the sodium and iodide ions are closely bound and that the interaction is effectively between Na atoms and NaI molecules. The $\overline{\Delta F}^E$, $\overline{\Delta H}$, and $\overline{\Delta S}^E$ values, shown in the sixth row of Table 3, are seen to be in good agreement with the ones measured experimentally. Other calculations showed that any attempt to account for coulombic interactions, assuming NaI to be ionized, leads to values more than an order of magnitude in error.

The following equation is recommended for calculating $\overline{\Delta F}^E$ and the activity coefficient, γ , of sodium iodide in sodium.

Figure 13. Partial molar excess free energy of mixing values for infinitely dilute solutions of NaI in Na. Values calculated from activity coefficients measured in vaporization experiments.

Table 3

Comparison of the Thermodynamic Properties of Sodium Iodine-Sodium Solutions^a

Method	$\overline{\Delta F}^E$ at 750°C, kcal/mole	$\overline{\Delta H}$, kcal/mole	$\overline{\Delta S}^E$, eu
Borelius power series	2.06	2.1	0.0
Henry's law	7.86	13.2	5.2
1 Parameter (Pitzer ^b)	8.06	14.2	6.0
2 Parameter (Present work)	8.14	15.3	7.0
Experimental (Present work)	8.94	15.9	6.7
Statistical mechanics average potential model	8.3	15.6	7.2

^aNaI at infinite dilution.

^bK. Pitzer, *J. Am. Chem. Soc.* **84**, 2025-8 (1962).

$$\overline{\Delta F}^E = RT \ln \gamma = 15,900 - 6.7T.$$

The chemical potential or the "escaping tendency" of a solute from a solution is directly related to its fugacity, f . At moderate pressures, the fugacity may be approximated by the partial pressure of the solute, P , using the expression

$$f \cong P = P^0 \gamma x,$$

where P^0 is the vapor pressure of the pure solute and x its mole fraction in solution. These partial pressures are useful for determining the static equilibrium distribution of a fission product between the vapor and liquid phases. The ratio of the partial pressures of fission products Cs, Rb, I as NaI, Te, Sr, and Ba to their mole fraction is plotted in Figure 14 as a function of reciprocal absolute temperature. The solid lines for all fission products except iodine were calculated from the above equation using published vapor pressure data and our $\overline{\Delta F}^E$ values deduced from the respective phase diagrams. In the case of iodine, the experimental $\overline{\Delta F}^E$ values were employed. The dotted lines, shown here for comparison, were calculated on the basis of ideal solution behavior. In some cases, the differences between the actual and ideal partial pressures are more than an order of magnitude.

Under the conditions of dynamic equilibrium vaporization, the fraction of a fission product vaporized, F_{fp} , is related to the fraction of the sodium vaporized, F_{Na} , by the equation

Figure 14. Fission product partial pressures over liquid sodium for the limiting case of infinite dilution. The dashed lines, based on ideal solutions, are shown for comparison.

$$F_{fp} = 1 - (1 - F_{Na})^A,$$

where

$$A = (P_{fp}^0 / P_{Na}^0) \gamma,$$

and P_{fp}^0 and P_{Na}^0 are the vapor pressures of the fission product and sodium, respectively. The parameter A is a function of temperature and can be expressed by the equation

$$A = ae^{b/T}.$$

Values of the constants, a and b , are given in Table 4 for Cs, Rb, Sr, NaI, Ba, and Sb. A comparison of the predicted and measured vaporization curves for the Cs-Na system is shown in Figure 15. The vaporization curves shown in Figure 16 for the NaI-Na system were calculated from the experimentally determined $\overline{\Delta F^B}$ value.

Another phase of this program was initiated to investigate the parameters controlling the rate of fission product cesium vaporization from sodium into a flowing gas stream. Experiments were carried out at 460°C employing both helium and argon as carrier gases. The fraction of cesium re-

Table 4

Constants for Calculating the Extent of Fission Product Vaporization as a Function of the Sodium Vaporized (Employing Equations in the Text)

Fission product	Temperature range, °K	a	b
Cesium	700–900	0.132	+5080
Rubidium	700–900	0.234	+4180
Strontium	700–1000	5.41	–5270
Iodine ^a	940–1200	0.37	–150
Barium	700–1100	2.18	–6770
Tellurium	725–1100	2.81	–10150
Antimony	903.7–1100	8.50	+19940

^aPresent as NaI.

maining in sodium is plotted in Figure 17 as a function of time. A comparison of the two curves shown in the figure indicates a small dependence of release rate on the molecular weight of the carrier gas. This is probably due to the existence of a small gas-phase resistance in addition to the diffusional resistance in the liquid phase.

TRANSPORT STUDIES

The transport of fission products from nuclear materials into the surrounding atmosphere constitutes a major consideration in the safety of a nuclear reactor. In this continuing study, analytical models as well as experimental measurements are being obtained in order to predict fission product release from molten fuels and claddings as a function of time, temperature, volume-to-surface ratio, and fission-product solubility in the condensed phase. Experimental measurements on the release rate of fission-product iodine from molten uranium into a flowing gas were completed during the year.

The percentage of iodine release as a function of time is shown in Figure 18 for three different uranium sample sizes. The data shown for liquid depths of 0.250 and 1.625 cm are the results of experiments employing helium as a carrier gas. These experiments were carried out at a flow rate of 200 cc/min and an average sample temperature of 1400°C. Data given for the 0.813-cm liquid depth represent the average of both helium and argon experimental results with flow rates varying from 100 to 1000 cc/min and sample temperatures ranging from 1200° to 1500°C. The average deviation of the data is shown by the brackets through

Figure 15. Vaporization curves for the Cs-Na system. The open and closed circles are experimental points; the solid curves were calculated from the information given in Table 4.

Figure 17. Vaporization of Cs^{137} from Na into a flowing gas stream. The data in the upper curve were obtained employing argon as a carrier gas; the data in the lower curve were obtained with helium.

Figure 16. Vaporization curves for infinitely dilute solutions of NaI in Na. These curves, based on experimental data, were drawn employing the constants given in Table 4.

the points plotted for the two shallower depth samples.

A mathematical expression for the transport of fission products was derived for the general case of solute diffusion in both the condensed and gaseous phases. The rate of transport across the vapor-liquid interface was expressed by the Langmuir equation for vaporization, generalized for non-ideal multicomponent solutions. The same general mathematical expression is applicable for the case of a desorption mechanism or a rate controlled by a first-order reaction at the interface.

Figure 18. Release of fission-product iodine from molten uranium for three liquid depth samples.

Because of the high volatility of iodine at elevated temperatures, the rate-controlling process for this system is solute diffusion in the condensed phase rather than in the gas phase. This is verified by the fact that the release rate depends on the liquid depth but not on the molecular weight of the carrier gas or the gas flow rate. The experimental results are adequately correlated with an analytical model considering only liquid-phase diffusion and an interfacial resistance term.

The equation for calculating the fractional iodine release, F_R , is as follows.

$$F_R = 1 - \sum_{n=1}^{\infty} \frac{2L^2 \exp(-\beta_n^2 Dt/l^2)}{\beta_n^2(\beta_n^2 + L^2 + L)}$$

where

- l = liquid depth, cm,
- D = diffusivity, cm^2/sec ,
- t = time, sec,
- $L = l\alpha/D$,
- α = a rate constant, cm/sec, representing the interfacial resistance term, and β_n 's are the positive roots of $\beta \tan \beta = L$.

This equation can be deduced from the general equation by neglecting the gas-phase diffusional resistance. Graphs showing F_R for several values of L have been given by Crank (*The Mathematics of Diffusion*, p. 56, Oxford Press, 1964) and are useful in making numerical computations.

A diffusivity of $2.65 \times 10^{-4} \text{ cm}^2/\text{sec}$ and a rate constant of $1.96 \times 10^{-4} \text{ cm/sec}$ were evaluated from the experimental results of the 0.813- and 1.625-cm liquid depth samples. With these values, the release curves for samples of all three liquid depths were computed and are shown as broken lines in Figure 18. Since the estimated Langmuir vaporization constant is larger than the observed interfacial resistance term, the nature of the actual rate process occurring at the interface is not certain. It may be due to the desorption of the fission product iodine from uranium or a chemical reaction of iodine with uranium at the surface to form a volatile uranium subiodide (A.W. Castleman, Jr. and I.N. Tang, Chemical considerations in fast reactor safety, in *Proc. Conf. Safety, Fuels, and Core Design in Large Fast Power Reactors*, Argonne National Laboratory, Oct. 1965, pp. 848-54, ANL-7120, 1966).

AEROSOL STUDIES

The nature and coagulation behavior of aerosols formed during the high-temperature vaporization of fast-reactor materials were investigated. The temperature of the materials being studied was rapidly raised above the melting point to simulate an accidental reactor power excursion. Individual studies were made with PuO_2 vaporized at 2800°C and UO_2 vaporized at 3000°C into both argon and nitrogen gases. In addition, combinations of vaporized PuO_2 - UO_2 and Na vaporized into moist air mixed with vaporizing UO_2 were studied.

A tantalum carbide (mp, 3882°C) resistance heater was developed to melt and vaporize UO_2 (mp, 2840°C) under controlled conditions. Heating to a temperature of 3200°C was accomplished

in a few seconds. This enabled a 50-mg sample of UO_2 to be completely vaporized in 30 to 45 sec. The generated aerosol was carried by a gas stream into an aging chamber. The aerosol was sampled periodically using a thermal precipitator with carbon-coated electron microscope grids. Three aging chambers of 1000, 18, and 6.6 liters in volume were used to obtain aerosols of varying mass concentration.

Typical UO_2 and PuO_2 agglomerates generated in argon are composed of cubic-shaped particles ranging in size from 40 to $400 \text{ \AA}$, connected in twisting chainlike patterns as shown in Figures 19 and 20. An aerosol with an initial mass concentration of $52 \text{ mg UO}_2/\text{m}^3$ produced an aggregate having a count median diameter (C.M.D.) of 0.083μ and a geometric standard deviation (σ_g) of 2.9 10 min after generation. After $1\frac{1}{2}$ hr, the mass concentration dropped to 3 mg/m^3 and the C.M.D. of the aerosol increased to 1.5μ .

A tenfold increase in initial mass concentration to $520 \text{ mg UO}_2/\text{m}^3$ produced an aerosol with a C.M.D. of 0.075μ at 2 min and a C.M.D. of 2.0μ at 25 min. The mass concentration of the aerosol was $130 \text{ mg UO}_2/\text{m}^3$ at 25 min. The C.M.D. dropped to a persistent 0.075μ as the mass concentration dropped to $17.5 \text{ mg UO}_2/\text{m}^3$. The highest mass concentration aerosol produced was $2.24 \text{ g UO}_2/\text{m}^3$. However, this aerosol persisted for <10 min and rapidly settled in a visible fume.

A typical $1\frac{1}{2}\text{-}\mu$ PuO_2 agglomerate (based on equal area measurement) was composed of cubic particles with a C.M.D. of 0.0118μ and a σ_g of 2.0. The apparent density of 0.101 g/cm^3 for this individual agglomerate was calculated using the theoretical density of PuO_2 for each individual particle. Typical photographs of the deposit are shown in Figures 21 and 22.

The results of several PuO_2 vaporization experiments are shown in Table 5. The C.M.D. of the aerosol was not observed to vary significantly with time in any of the runs; however, the standard deviation was found to increase with increasing initial mass concentration. The coagulation constant during the first few hours of aging was about $10^{-8} \text{ cm}^3/\text{sec}$, but appeared to increase by a factor of eight after 24 hr.

A mixture of sodium and UO_2 aerosols was produced by vaporizing sodium metal and UO_2 in nitrogen. The mixed aerosol was carried by the nitrogen gas stream into an 18-liter settling chamber. The results, given in Table 6, show that the

Figure 19. Aggregates of cubic UO_2 aerosol particles. Mass concentration of aerosol, $1.2\ \text{g}\ \text{UO}_2/\text{m}^3$; sampled 10 min after generation. Electron micrographs of thermal precipitator grids.

Figure 20. Aggregates of cubic PuO_2 aerosol particles. Mass concentration of aerosol, $13\ \text{mg}\ \text{PuO}_2/\text{m}^3$; sampled 10 min after generation.

Figure 21. PuO_2 aerosol aggregates at a mass concentration of 0.5 mg Pu/m^3 ; sampled 1 hr after generation.

Figure 22. PuO_2 aerosol aggregates of Figure 21 after 71 hr, dropping to a mass concentration of $2.9 \times 10^{-4} \text{ mg Pu/m}^3$.

Figure 23. Aerosol of sodium in UO_2 aggregates in argon gas; sampled immediately after generation. Dark chain is UO_2 , light spheres in chain are Na.

Figure 24. Aerosol of sodium spheres in UO_2 aggregates in argon gas; sampled immediately after generation. Dark chain is UO_2 , light spheres in chain are Na.

Figure 25. Aerosol of sodium spheres in UO_2 aggregates in air at 23% relative humidity; sampled immediately. Electron micrograph of thermal precipitator grids.

Figure 26. Aerosol of sodium spheres in UO_2 aggregates in Figure 25; sampled at $1\frac{1}{2}$ hr.

Table 5
PuO₂ Aerosols in Nitrogen Gas

m (mass concentration), mg PuO ₂ /m ³	t (time after vaporization), hr	C.M.D. (count mean diameter), μ	σ_g (geometric standard deviation)	K (coagulation constant), cm ³ /sec $\times 10^{-8}$
15	0.17	0.152	1.91	
1.0	1	0.153	1.78	
0.20	2	0.147	1.87	
0.15	7	0.166	1.80	0.65
0.026	24	0.151	2.47	1.6
29	0.083			
0.29	2	0.208	1.90	
0.073	6	0.201	1.79	2.6
0.029	23	0.306	1.64	4.1
0.0033	71	0.218	1.97	8.5
135	0			
6.0	4	0.239	2.35	
2.6	5	0.553	2.32	1.4
112	0			
6.0	4	0.208	2.12	
3.0	6	0.301	3.02	0.28
0.037	50	0.135 ^a	1.67	
31	0.083	0.167	1.87	
0.054	24	0.281	1.71	2.6
0.007	72	0.247	1.62	8.6
6.1 ^b	0.083			
0.09	4	0.250	1.77	
0.085	6	0.339	1.75	1.0
0.040	24	0.312	1.80	0.7
0.037	28	0.280	1.71	7.2
0.023	48	0.298	2.15	7.4
0.020	54	0.273	1.79	2.5

^aCumulative aerosol deposited on bottom of chamber.

^bConcentration of PuO₂ in a 20% PuO₂-80% UO₂ mixture.

C.M.D. of both the Na and the UO₂ aerosols remained below 0.2 μ with $\sigma_g < 1.75$. However, the sodium that deposited on the wall after 2 hr was composed of larger particles with a C.M.D. of 1.08 μ . Pictures of the cubic UO₂ particles and sodium spheres are shown in Figures 23 and 24, respectively. A sample taken 1½ hr after generation revealed that no particulates of Na or UO₂ remained in the gas at this time. A comparison of this rapid agglomeration with the slower agglomeration noted for pure UO₂ and discussed above indicates the apparent scavenging effect of sodium.

A UO₂-Na mixture was also generated in air at 23% relative humidity. A cluster of sodium oxide spheres intertwined in chains of UO₂ particles, as shown in Figure 25, was also observed in this study. After 1½ hr, the few remaining aerosol particles were composed of 0.1- to 0.7- μ agglomerates of sodium oxide and UO₂. The photographs of these are shown in Figure 26.

Table 6
Behavior of a UO₂ Aerosol
in Sodium Vapor and Nitrogen With Time

	C.M.D., μ	σ_g
Immediate UO ₂	1.177	1.46
Immediate Na	0.199	1.53
30-min UO ₂	0.153	1.43
30-min Na	0.192	1.75
1½ hr	No particles	
Wall UO ₂	0.165	1.67
Wall Na	1.08	1.41

CHEMICAL STATE OF IODINE RELEASED INTO STEAM

Methyl iodide has been found to be one of the species formed during the release of iodine from UO₂ into steam-air mixtures. Its stability in a combined oxidizing and radiation environment

was studied. Samples of CH_3I -air mixtures were irradiated at 55° to 60°F with Co^{60} γ rays. A summary of the results is shown in Figure 27, where the percentage of CH_3I remaining is plotted vs the total absorbed dose in rads.

The following simple reaction mechanism successfully explains the CH_3I decomposition results.

Here M designates an air molecule (either oxygen or nitrogen), and M^* is an excited molecule capable of transferring its excitation energy to a CH_3I molecule. The peroxide radicals produced in step (3) may react with either NO or NO_2 to form CH_3ONO or CH_3ONO_2 , which are indeed the observed radiolysis products.

Applying steady-state hypothesis leads to the following equation:

$$-(dx/dt) = (k_1 k_2 x) / (k_{-1} + k_2 x),$$

where x is the concentration of CH_3I and $-(dx/dt)$ is the rate of CH_3I decomposition at constant air pressure, temperature, and gamma intensity. At low CH_3I concentrations where $k_2 x \ll k_{-1}$, the above expression reduces to a first-order rate equation, which is in agreement with our findings for the concentration range 10^{-8} to $10^{-6} M$ reported previously. At higher concentrations where the above mechanism still holds and $k_2 \gg k_{-1}$, we ob-

Figure 27. Decomposition of CH_3I in air during γ irradiation. Curves are shown for three regions of initial CH_3I gas-phase concentration.

tain a zero-order rate equation which predicts a straight line for a plot of percentage CH_3I remaining vs total absorbed dose. The straight line shown in Figure 27 was obtained for the initial CH_3I concentration of $2.4 \times 10^{-4} M$.

For the intermediate case where $k_2 x$ is comparable to k_{-1} , the above equation can be integrated and rearranged to give

$$-\ln[f/(1-f)] = (\beta k_2/k_{-1})[It/(1-f)] + (k_2 x_0/k_{-1}),$$

where

f = fraction of CH_3I remaining,

x_0 = initial CH_3I concentration,

I = gamma intensity, rads/hr,

It = total absorbed dose, rads, and

β = a proportionality constant defined by $k_1 = \beta I$.

A plot of $-\ln[f/(1-f)]$ vs $It/(1-f)$ should give a straight line as shown in Figure 28. The values of β and k_2/k_{-1} can be calculated from its slope and intercept.

Figure 28. Decomposition of CH_3I for samples of $4.5 \times 10^{-5} M$ initial gas-phase concentrations.

High-Temperature Distillation of Sea Water

L. HATCH

Present-day plans for large-scale production of potable water from the sea are widely based on the well-developed technology of multistage flash distillation. A basic and long-standing problem in sea water distillation, however, stems from an upper temperature limitation which is generally imposed to avoid the formation of solid deposits or "scale" on the walls of the heat transfer tubes (saline water is heated on one side of the tube as steam condenses on the other side). This is due to the inverted solubility-temperature relationship for some of the salts, notably calcium sulfate.

Since the presence of scale is highly detrimental to the transfer of heat across the tube wall, which is at the heart of the process, the upper temperature is generally limited to about 250°F. Elimination of the scaling problem would permit the use of higher temperatures which, in turn, would result in higher thermal efficiency, or larger amounts of fresh water produced per unit quantity of heat energy supplied.

A new approach to the scaling problem, under investigation at Brookhaven National Laboratory during the past two years, offers good promise for practical application. The principle involved is to maintain a "fluidized" bed of granular material, about 1/8 in. in diameter, in a vertical heat exchanger with the particles held in suspension in the upward-flowing saline water on one side of the tubes. For a number of reasons the motion of the particles interferes with the formation of scale at the high temperatures and causes the solids that deposit from solution to be present as small crystals in the saline water and not on the walls of the tube.

During the past year fluidized-bed heat exchangers have been operated over extended periods with natural sea water at temperatures as high as 400°F with complete absence of scale.

Engineering Assistance

The Engineering Assistance Group of the Engineering Division is a service organization supporting departmental research programs. About 30 persons are involved in engineering, design, and construction of experimental equipment. The

group also contributes to ANS and ASME committees and the *High-Temperature Liquid-Metal Technology Review*.

A fast source assembly and a plutonium exponential experiment were designed and fabricated for the Reactor Physics Experimental Group during the report period. Also, a pulsed reactor critical assembly was designed and is now being fabricated. An automatic gamma counting pig is now being designed.

The group has played an active part in the modifications being made to the reactor cooling tower system. The system is being modified to isolate all cooling water from the ground water in the event the cooling tower water becomes contaminated with HFBR primary heavy water, and it is also being modified to control the quantity of make-up water being used. Design work has been completed (by Burns & Roe, Inc., under BNL direction) and field construction will be finished early next year.

A major effort on the Chemonuclear In-Pile Research Loop (CIRL) continued through the summer, after which a reduction in the program took place. Design work is complete and all major components, except for shielding, are installed. Testing of electrical control circuits and loop components is under way.

Design and engineering work on irradiation facilities was extensive. The enlargement and unification of the recessed gamma cells and the gamma process tank facilities were completed. A two-truck loading dock annex and conveyor extension were completed for the High Intensity Radiation Development Laboratory (HIRDL). Designs for the Brookhaven Portable Cesium Development Irradiator and the Pakistan Research Irradiator were sent to the New York Operations Office of the AEC. Maintenance inspections of the research irradiators at MIT and the Universities of California, Florida, and Washington were completed. A design study has begun on a blood irradiator that will treat four animals simultaneously.

Two new test sections have been designed for use in the pumped sodium test loops. The design of a high heat flux pumped sodium loop was completed, and work continues on the test section for this facility.

A new vapor generator has been designed for the boiling potassium heat transfer facility. Design work, begun last year, on a condensing potassium loop was halted and the effort shifted to modifying

the NaK heat transfer facility. The single-phase 1000°F NaK facility is being rebuilt to allow boiling inception and steady boiling investigations with sodium up to 1600°F. Major components have been designed and facility renovations have begun.

A study was completed on the proposed conversion of the BGRR to a water-cooled, pressure-tube type reactor. Contributions were made to various reactor evaluations, in particular the evaluation of the molten salt reactor.

As an outgrowth of research done at BNL on hydrogen storage, a study of the application of this principle to the propulsion of automobiles was completed.

General instrumentation support, including design and construction of panels and control systems, has been given to departmental programs.

Pulsed Research Reactor Study

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Conceptual design studies of alternate fast reactor systems previously reported, and analysis of their limiting parameters, have led to the definition of the research and development effort required to meet design goals. The two alternative concepts under consideration as sources for neutron beam experiments are a pulsed reactor in which the reactivity is periodically pulsed into the superprompt

Figure 29. Temperature history of nodes at the axial peak of the hot pin during and following a power pulse.

critical region by mechanical means and an accelerator-injected pulsed reactor where the reactivity pulsing to a subprompt critical condition coincides with the injection of neutrons from an electron accelerator source. The effort during this year has involved the development and application of analytical design techniques and an experimental program. Analytical techniques were developed for thermal, stress, and physics calculations while the experimental program has been directed toward testing of fuel materials, a critical experiment, and pulsed neutron time-of-flight measurements.

THERMAL AND STRESS ANALYSIS

The rapid variation in heat generation (30-MW time-averaged power and 20,000-MW peak in the case of the pulsed reactor) requires the capability to calculate the transient temperature distribution in the fuel elements and coolant. A 3-dimensional, transient heat transfer code (LION) for the CDC 6600 has been obtained from Knolls Atomic Power Laboratory (KAPL) and adapted for use at BNL.

Figure 30. Transient temperature profiles at the axial peak of the hot pin at various times following a power pulse.

Calculations have been made for some representative fuel systems. The code has been used to follow the temperature distribution of the core hot pin from uniform initial temperature to the equilibrium temperature cycling condition after many pulses. The code has been modified to provide most of the information required directly as input for another code that calculates the thermal stress distribution in the fuel pin.

Figures 29 and 30 show the temperature history in a typical pulsed reactor core following a 60- μ sec pulse at equilibrium pulsing conditions with a repetition rate of 22 pulses/sec. The fuel element is a 0.125-in. pin of 60 vol % UO_2 -Mo cermet with a metallurgically bonded 0.015-in.-thick Mo cladding. Figure 29 is a plot of the temperatures of each nodal point at the axial peak of the core hot pin. Nodes 51 through 57 cover the fuel from centerline to surface; nodes 58, 59, and 60 are in the cladding; node 106 is on the cladding surface; and node 117 is in the coolant stream. The fuel temperature increases at a rate of 2×10^6 $^\circ\text{F}/\text{sec}$ for ≈ 70 μsec after the start of the pulse while the clad remains unaffected for this period. The rapid chilling of the outer portion of the cermet, node 57, as a result of heat loss to the high thermal conductivity clad, is illustrated by the decrease in temperature indicated after ≈ 180 μsec . This chilling effect causes a steep temperature gradient at the fuel-clad interface and leads to a significant alternating thermal stress component that must be added to the thermal stress that exists because of

the steady-state temperature gradient in the pin. The peak thermal stress at the fuel-clad interface should occur after the inertial stress waves, caused by the inability of the fuel to expand in equilibrium with the rapid temperature increase, have been damped out. Figure 30 shows the actual temperature profile in the pin as a function of time, and indicates the steep temperature gradient in the vicinity of the fuel-clad interface after 216 μsec . The maximum gradient actually occurs at 192 μsec and stresses were calculated at that time. After 45 msec, all temperatures have returned to their initial values indicating an equilibrium pulsing condition at the repetition rate of 22 pulses/sec.

The results of the transient thermal analysis were used as input to a code written for the CDC 6600 to calculate the stress pattern in the clad UO_2 -Mo fuel pin. The radial (σ_r), circumferential (σ_θ), and axial (σ_z) stresses corresponding to the temperature pattern at the time of the peak temperature gradient at the fuel-clad interface were determined and are plotted in Figure 31. The clad is in tension in the circumferential and longitudinal direction and serves to maintain a compressive stress in most of the fuel. The stress at the fuel surface is tensile and the magnitude of this stress can be controlled to some extent by variation of the cladding thickness. The stresses in the fuel include an average thermal stress that is due to the steady-state temperature gradient, as well as alternating stress components that are due to chilling and inertial effects. The calculated stresses cannot be related to a failure analysis, since there are no high cycle fatigue data available on the fuel material. The bulk of the testing in the fuel development program is directed toward obtaining these data.

As a result of the analysis of a UO_2 -Mo cermet fuel clad with molybdenum, it was apparent that the use of a clad with a lower thermal conductivity, such as Inconel, might offer some advantage in reducing the chilling effect at the fuel surface. The same advantage could be realized by means of a ceramic insulating barrier; however, the resulting restraint of the fuel axially by the clad would not be as satisfactory. Analysis of the UO_2 -Mo cermet clad with Inconel indicates that the fuel surface tensile stresses are reduced by a factor of 2. Most of this reduction is due to the decreased surface chilling effect while the balance is the result of a better match between the $E\alpha$ parameter of the fuel and clad.

Figure 31. Thermal stresses in fuel pin at time of the peak thermal gradient.

The stress analyses conducted do not include effects of circumferential temperature variations or end conditions. Solutions including these effects can be obtained by the application of a finite element code that is being developed. This code has been verified by comparison with some sample stress problems that have been solved analytically.

ANALYTICAL PHYSICS

Survey calculations were made for the core design of the critical experiment. The criticality conditions and prompt neutron lifetimes for various core compositions and geometries were determined and will be checked against experimental results obtained from operation of the critical experiment. The use of poison materials in the form of core liners, to reduce the prompt neutron lifetime, has been considered and analytical techniques for calculating their effect will be verified in the experiment.

Considerable attention has been given to methods of improving the pulse characteristics of a reactor system. A simple relationship between pulse width and reactor design parameters, assuming a parabolic reactivity curve, is given by:

$$\theta \approx (\tau/\alpha V^2)^{1/3},$$

where

- θ = pulse width at half power, sec,
- τ = prompt neutron lifetime, sec,
- α = parabolic coefficient, m^{-2} , and
- V = velocity of moving reflector section, m/sec.

This relationship offers an incentive to operate at high reflector velocities; however, further studies have indicated that the reactivity curve may be more nearly linear and in this case the following relationship holds:

$$\theta = 2.35(\tau/\alpha' V)^{1/2}$$

where α' = linear coefficient, m^{-1} . Thus, the incentive for reducing the prompt neutron lifetime and increasing the α coefficient of reactivity appears to be equal to that for increasing the reflector velocity.

In the larger cores (30 to 60 liters) being considered for the pulsed reactor, methods of increasing the value of the coefficient of the reactivity curve, α , are being studied. Cavities of various geometries in the bare face of the core can enhance the neutron leakage toward the moving reflector. If the remaining portion of the bare core face is lined with poison material, very steep flux gradients

can be produced at the edges of the cavity with corresponding large values of α obtained for the reactivity pulse when the reflector moves past the cavity. Various analytical methods have been used to determine the shape of the reactivity curve as a function of position of the reflector. S_N methods have been used, but this technique is not reliable in cases of strong neutron anisotropy. A collision probability method is being developed and the ORNL Monte Carlo code o5R has been obtained and is being prepared for the IBM 7094.

FUEL DEVELOPMENT PROGRAM

Fuel materials with a moderate uranium loading of ≈ 6 g U/cm³ may be used in a pulsed reactor, while a higher loading of ≈ 12 g U/cm³ is required to fuel the more compact accelerator-injected pulsed reactor core. A fuel development program is required for either system in order to demonstrate the ability of candidate fuel materials to withstand the stresses resulting from the rapid variation of temperature in the fuel in the pulsed mode of operation. The pulse repetition rate desired and the economic necessity of achieving a significant fuel burnup during the life of the core lead to the requirement for high-cycle fatigue data on irradiated fuel materials. A three-phase fuel development program has been outlined and may be summarized as follows:

- Phase I—Survey and screening tests of unirradiated candidate fuel materials.
- Phase II—Irradiation and test of selected fuel materials.
- Phase III—Proof tests of selected fuel materials in fuel element form.

The survey portion of Phase I has been completed, specimens of candidate fuel materials have been made, and testing is in progress.

Battelle Memorial Institute has performed the survey of fuel materials with the following guidelines:

1. A minimum of about 3.5 g/cm³ of fissile material,
2. A capability of 2% burnup,
3. Minimum amounts of elements with low atomic number to provide for a short prompt neutron lifetime,
4. Suitability for operation at a surface temperature of about 400°C at a power density of 2 to 4 MW/liter of fuel, and

5. Sufficient mechanical strength so that tensile and fatigue testing can be performed on unclad specimens.

The fuels with these characteristics for which data on physical and mechanical properties were found included alloys, dispersions, and cermets. The alloys considered were U-Mo, U-Nb, U-Zr, U-Pd, and U-Nb-Zr. None of the plutonium-bearing alloys seemed to be very promising. The dispersions considered were U-Th and U-Yb, and the cermets considered were UN in matrices of chromium, tungsten, and molybdenum, UC in tungsten and molybdenum, and UO_2 in chromium, niobium, stainless steel, tungsten, and molybdenum. The substitution of plutonium for uranium is possible for most of these cermets but few data are available on such systems. For the purposes of the Phase I test program, it is being assumed that the substitution of plutonium for uranium has no effect on cermet mechanical properties. In addition to these alloys, dispersions, and cermets, clad ceramic fuels such as UO_2 , UN, UC, PuO_2 , and PuC are being considered; however, no meaningful tests on these systems can be conducted under the scope of Phase I work. As a result of the survey, the following fuel systems were selected for fatigue testing under an unirradiated condition (Phase I): (1) U-10% Mo alloy, (2) U-31% Nb-12% Zr alloy, (3) U-62% Nb-7% Zr alloy, (4) UO_2 -stainless steel cermet, and (5) UO_2 -Mo cermet.

In addition, fabrication development work and tensile testing will be performed on the U-Th dispersion and a U-20% Nb-27% Zr ternary alloy. Several promising systems that also require fabrication development may be pursued in the future; these are U-50% Nb alloy and cermets with a fissile matrix of U-80% Nb or U-60% Pd.

The alloy fuel U-10% Mo was selected on the basis of its high uranium loading and the large amount of available data and experience with the material. Its fissile loading makes it the only fuel among those listed that could be used in a small core for the accelerator-injected pulsed reactor. The U-Nb-Zr ternary alloys exhibit a stable gamma phase in the composition range indicated, a desirable characteristic in a pulsed reactor fuel. The UO_2 -stainless steel cermet system is relatively well developed and should have better burnup potential than that of the alloy fuels. Specimens of these fuel systems have been fabricated by Battelle for fatigue testing. Some tensile testing is planned

for the ternary alloys to fill gaps in the data. The UO_2 -molybdenum cermet fuel looks especially promising because of the properties of the molybdenum matrix. The high thermal conductivity, low Young's modulus, and low coefficient of thermal expansion of this cermet combine to give a low thermal and inertial stress parameter. A total of 90 specimens of this cermet, including 48 for fatigue testing, were fabricated at the General Electric Nuclear Materials and Propulsion Operation. The samples covered a range of fuel loading from 40 to 80 vol % and particle sizes of 40, 150, and 400 μ , and were made both in the clad and unclad form. Measurements were made of the tensile strength, thermal expansion, thermal conductivity, and sonic velocity in this material. The results of the tensile tests conducted on the UO_2 -Mo cermet system are summarized in Table 7.

Fatigue testing is to be conducted mechanically at 80 cps and ultrasonically at 14.2 kc/sec at a temperature of 800°F. The test temperature for the U-10% Mo will be lower to prevent phase transformation due to temperature. The effect of the cyclic stress on the phase transformation will be evaluated. Two ultrasonic tests have been conducted on 60 vol % UO_2 -Mo cermet specimens with a particle size of 150 μ . One specimen had an 0.005-in.-thick molybdenum cladding and the cladding was removed from the other. Both were tested at a calculated mean stress of 4200 psi and an alternating stress of 950 psi. The clad specimen failed after 5.18×10^8 cycles while the unclad specimen had not failed when the test was terminated at 10^9 cycles. The failed specimen was examined metallographically and it was noted that the UO_2 particles were poorly distributed in the cermet; the cladding-to-fuel bond was excellent. The fuel manufacturer attributes the poor UO_2 distribution to the method of loading the UO_2 -Mo powder blend into the molds prior to isostatic pressing of the rods. The tubular molds of large L/D required tamping of the powder blend into the mold as each small addition was made. Apparently this tamping caused separation of the molybdenum coating from the fuel particles and the coarser UO_2 particles became more concentrated at the top of each tamped layer.

Because of uncertainties in the method used to calculate the stress conditions in the ultrasonic fatigue testing of clad composite materials, a series of strain gage tests are planned. These tests will be conducted on stainless steel specimens in order

Table 7
Tensile Test Results for Mo-UO₂ Cermet Specimens in Helium

Specimen No.	Fuel loading, vol %	Fuel particle size, μ	Room temperature static modulus, $\text{psi} \times 10^{-6}$	Test temperature, °F	Static modulus at temperature, $\text{psi} \times 10^{-6}$	Yield stress, ^a $\text{psi} \times 10^{-3}$		Ultimate stress, ^b $\text{psi} \times 10^{-3}$	Elongation, ^b %
						0.02%	0.2%		
C-1-a1	80	150	14.2	800	—	3.6	—	4.6	0.1
C-1-a2	80	150	—	800	—	4.4	—	4.6	0.3
C-1-a3	80	150	—	800	9.8	3.9	—	4.4	0.2
A-1-a4	60	150	12.1	1500	—	6.6	—	7.2	1.1
A-1-a5	60	150	—	1500	—	—	—	6.9	0.6
A-1-a6	60	150	—	1500	19.7	—	—	12.9	0.1
A-1-a1	60	150	17.4	800	14.17	8.3	—	10.3	0.6
A-1-a2	60	150	—	800	10.6	—	—	12.6	0.3 ^c
A-1-a3	60	150	6.5	800	—	5.3	7.8	7.9	0.6
A-2-a1	60	40	20.5	800	—	—	—	13.5	0.3
A-2-a2	60	40	—	800	—	—	—	10.2	0.4
A-2-a3	60	40	—	800	—	—	—	13.7	0.2
A-1-a7-G ^d	60	150	14.3	800	—	—	—	10.5	0.2
A-1-a8-G ^d	60	150	—	800	10.4	—	—	10.4	0.1
A-1-a9-G ^d	60	150	—	800	11.5	—	—	11.5	0.4
A-1-b1 ^e	60	150	15.4	800	—	8.5	11.5	13.3	1.1
A-1-b2 ^e	60	150	—	800	—	—	—	16.6	1.1
A-1-b3 ^e	60	150	—	800	20.2	8.9	11.1	13.6	1.7
A-1-c1 ^{f,g}	60	150	—	800	—	9.2	—	11.2	0.5
A-1-c2 ^f	60	150	18.2	800	7.5	8.2	—	10.9	0.5
B-1-a1	40	150	15.4	800	—	8.1	11.5	15.1	2.9
B-1-a2	40	150	—	800	—	12.6	15.0	17.1	2.4
B-1-a3	40	150	—	800	10.4	9.2	11.6	14.3	1.2
A-3-b1	40	400	14.0	800	—	7.9	10.6	12.4	1.9
A-3-b2	40	400	—	800	—	9.5	11.5	14.9	3.0
A-3-b3	40	400	—	800	—	8.8	11.2	13.7	1.2
D-1	0	—	48.5	800	—	7.1	10.1	37.8	52 ^d
D-2	0	—	—	800	—	7.3	9.8	37.7	53 ^d
D-3	0	—	—	800	—	7.7	9.9	36.8	51 ^d

^a0.005 min⁻¹ strain rate.

^b1.0-in. gage length $\times$ 0.25-in. diam.

^cBased on over-all length of specimen.

^dG=General Electric Mo; all other specimens are Sylvania Mo.

^eVapor coated with 0.005-in. Mo.

^fClad with Mo by autoclaving and machined to 0.003-in. thickness.

^gCladding removed from half of gage length in machining (because of nonconcentricity).

to develop methods of attachment for ultimate use on the fuel specimens to obtain a direct indication of the stress conditions. The ultrasonic fatigue testing method is of considerable interest, since a test can be conducted to 10⁹ stress cycles in 20 hr at 14.2 kc/sec while the same test requires 145 days at the mechanical testing frequency of 80 cps. Also, the strain rate characteristic of the ultrasonic test

is equivalent to that indicated for a pulsed reactor fuel.

CRITICAL EXPERIMENT

A fast reactor critical assembly has been designed for experiments in support of the design studies of the Pulsed Fast Research Reactor. This

assembly, which has a core of uranium, stainless steel, and aluminum, is being constructed in one of the centrally located critical assembly bays. The assembly will be used to test and refine the theoretical predictions for reactors made of these materials, as well as to study many effects not easily obtained from theory. In the initial experiments, the effects of two kinds of variation of the reflector will be studied. The first variation is the effect of local substitution of reflector material on emergent neutron beams; the second variation is the effect on the reactivity produced as reflector blocks are moved across a bare face of the core.

Survey calculations indicate that a core containing 26 vol % 93%-enriched uranium, 41 vol % steel, and 14 vol % aluminum will require about 150 kg of U^{235} to achieve criticality. A core of this composition is the first to be assembled. It approximates one version of a reference design with the sodium in the core replaced by aluminum of reduced density.

Most of the components of the assembly were made in the staff shop of the Experimental Reactor Physics Group. Other components requiring elaborate machining were made by the Central Shops. Construction is essentially complete, and it is expected that the assembly will become critical early in November.

TIME-OF-FLIGHT EFFECTS IN PULSED NEUTRON MEASUREMENTS

In the course of measurements of the rate of neutron decay in a moderator that was placed on an elevated platform in a sheet metal building to minimize "room return" effects, the observed decay rates were seen to depend on the location of the external neutron detector. Elementary calculations have now been made; they show that the measured decay constant should have this dependence even when the distance from the detector to the assembly is small. The calculations probably underestimate the importance of minimizing source-to-detector distance, since a point source and a point detector have been assumed instead of a more realistic extended source and a detector of finite size. The results show that the deduced decay constant depends on the interval of time during which decay is followed after the end of the pulse, and that the decay constant averaged over any such interval is always greater than the true value. All past measurements of neutron decay

rates in which the counters were outside the moderator may be subject to error because of these time-of-flight effects.

These effects of finite flight path indicate a possible origin of the hitherto unexplained dispersion in reported values of diffusion cooling parameters, the lack of agreement between measured decay constants in assemblies having equal geometric buckling but differing height-to-diameter ratios, and the inability to eliminate "room return" neutrons.

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