BROOKHAVEN NATIONAL LABORATORY

Annual Report

Nuclear Engineering Department

December 31, 1968

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BROOKHAVEN NATIONAL LABORATORY

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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, radiation application, and nuclear medicine. 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, direct conversion concepts, and radioisotopes for medical application.

The engineering and evaluation studies and the safeguarding of nuclear materials, 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.

P.F. Palmedo was an invited speaker at the AMU-ANC Conference on Fast Reactor Physics at Argonne National Laboratory, August 1968.

J. Chernick left in September for six months to visit the Puerto Rico Nuclear Center of the University of Puerto Rico at Mayaguez to lecture and consult with the staff on reactor physics research problems.

S. Pearlstein was appointed Director of the National Neutron Cross Section Center effective August 1, 1968.

B.A. Magurno presented an invited paper, entitled A Compilation of Neutron-Induced Threshold Reactions, at the Conference on the Use of Small Accelerators for Teaching and Research which was held in Oak Ridge, April 8-10, 1968.

M.D. Goldberg was invited to speak at the Nuclear Physics Seminar which was held at Brown University on March 21, 1968; his talk was entitled Collective Excitations Via Inelastic Deuteron Scattering - Nickel and Zinc Isotopes. He also participated in a meeting of Managers of Physics Information Analysis Centers held at the American Institute of Physics, New York City, on February 16, 1968.

S. Pearlstein participated in a meeting of the four Nuclear Cross Section Information Centers (IAEA, Vienna; ENEA, Saclay; Obninsk, USSR; National Neutron Cross Section Center, BNL), which was held in Vienna, February 16-18, 1968.

A. Prince presented a seminar at Savannah River Laboratory, March 29, 1968, on the Nuclear Properties of Transuranium Isotopes.

The Nuclear Materials Division was established January 19, 1968, as a new division headed by H. J.C. Kouts; its purpose is to assist the US AEC in its programs related to the safeguarding of nuclear materials.

W.A. Higginbotham visited the Nuclear Research Institute at Karlsruhe, Germany, during June and August 1968, to observe a safeguards experiment being conducted at a fuel processing plant.

L. Green returned to the Laboratory after an absence of two years during which time he was with the IAEA in Vienna. He served with the Agency as Senior Officer with the Economic Section of the Nuclear Power and Reactor Division. Participating in many international reactor economics meetings, he also was involved in giving assistance to developing countries interested in entering the nuclear power field.

K. Downes was invited to serve on an IAEA Panel on Revision of Safe Operations of Critical Assemblies and Research Reactors, held May 20-24 in Vienna. Just prior to the Vienna meeting,

he visited Harwell, England, for discussions with staff members.

F.T. Miles attended an IAEA Panel on Safeguards Methods for Reactors in Vienna, September 16-20, 1968.

B. Manowitz served as chairman of a meeting at BNL held in November 1968 under the Japanese-US information exchange agreement on the radiation-produced polyethylene and chemonuclear programs. The Japanese delegation was headed by Dr. K. Manekata, Chairman of the Japan Atomic Energy Research Institute, and by S. Sawayanagi, Director of the Takasaki Laboratory, and was made up of personnel from the JAERI laboratories at Takasaki and Tokai.

A meeting on the exchange of information on radiation processing applications between representatives of the US AEC and the Atomic Energy of Canada, Limited, was held at BNL under the auspices of the Radiation Division in December 1968.

Information meetings were also organized for the US AEC and held in October at BNL on concrete polymer materials and in November 1968 on the Atmospheric Sulfur Pollutants Program. The concrete polymer meeting was attended by representatives of the US Bureau of Reclamation, Bureau of Public Roads, Office of Saline Water, Dept. of Agriculture, and the Army Corps of Engineers, as well as the US AEC's Division of Isotopes Development. This meeting included people from the National Air Pollution Control Administration, New York City Dept. of Air Resources, New Haven Health Dept., Consolidated Edison of New York, Long Island Lighting Co., Pennsylvania Electric Co., United Illuminating Co., Mid-Island Air Service, and the Division of Biology and Medicine, and of Isotopes Development of the US AEC.

F.X. Rizzo served as Technical Coordinator for the Third Dosimetry Workshop, held at the National Bureau of Standards, Gaithersburg, Maryland, in April 1968, which was attended by experts from 60 different universities, governmental agencies, and private companies. He also chaired the subsequent meeting of the ASTM's Gamma Dosimetry Section of the Joint Subcommittee for Radiation Effects on Plastics and Dielectrics. This group is engaged in establishing international standards for all the gamma and charged-particle dosimeters currently in use.

G. Adler organized and chaired an International Symposium sponsored jointly by BNL and

the N.Y. State University at Stony Brook on Organic Solid State Chemistry in March 1968. It was attended by 85 scientists from the US and abroad.

J.W. Sutherland presented an invited paper, entitled The Radiolysis of Nitrous Oxide in the Adsorbed State, at the Fifth Miller Conference on Radiation Chemistry, Kazimierz, Poland, July 1968.

G. Adler presented an invited paper before a meeting of the British High Polymer Research Group at Morton-Hempstead, Devonshire, Great Britain, and he was made a Corresponding Member of the group.

L.E. Kukacka presented an invited paper, entitled The Use of Gamma Radiation to Initiate Polymerization Reactions, at the Fifth Pacific-Northwest Plastics Workshop held at the Washington State University, Pullman, Washington, in June 1968.

J.H. Cusack visited the Atomic Energy authorities in Santiago, Chile, and Buenos Aires, Argentina, June 1968, to arrange for the loan of Brookhaven Portable Cesium Development Irradiators to these countries.

F.B. Hill represented the US at a meeting of the International Standards Organization's working group on the International Nuclear Glossary, held in West Berlin, in May 1968.

The appointments of S. Sato (JAERI Laboratory at Tokai-mura) working on chemonuclear problems and R. Gabarain (Argentine AEC) working on polymer chemistry, both under the direction of M. Steinberg, have been extended.

L.H. Shendalman presented a paper by F.B. Hill and himself, entitled Thermal Stability of Batch Reactors for Photoinitiated Chain Reactions, at the Fourth European Chemical Reaction Engineering Symposium, held at Brussels, Belgium, in September 1968.

B. Manowitz presented an invited paper, entitled Use of Isotope Tracer Techniques in Studying the Fate of Air Pollutants, at the 1968 Annual Meeting of the American Nuclear Society held in Toronto, Canada, in June 1968.

M. Steinberg gave an invited paper as part of the Symposium on Radiation Processing at the American Chemical Society Meeting in Atlantic City, N.J., in September 1968.

M. Enusal spent five months at BNL as Guest Associate Chemist from Middle East Technical University, Ankara, Turkey, working in x-ray diffraction under the guidance of G. Adler.

L. Newman presented invited papers at the International Conference on Coordination Chemistry at Haifa and Jerusalem, Israel, September 16-18, 1968.

L. Newman continued as an active member of the Sodium Impurities Committee of the Sodium Components Development Program Working Group (a formally constituted advisory group to the US AEC).

S.W. Feldberg authored an invited chapter on digital simulation, entitled A General Method for Solving Electrochemical Diffusion-Kinetic Problems, for the book *Advances in Electroanalytical Chemistry*, A.J. Bard, Editor, M. Dekker, New York (in press).

M. Hillman presented an invited talk on combinatorial calculations of nuclear level densities at the Gordon Research Conference on Nuclear Chemistry, New London, New Hampshire, June 1968.

P. Richards co-authored a paper on analysis of the optimum conditions for data display and image perception in photoscanning presented at the IAEA Symposium on Medical Isotope Scintigraphy, Salzburg, Austria, August 6-15, 1968.

M. Luis Muga returned to the faculty of the University of Florida after a one-year appointment in the Isotopes Research Group, and J. Gilat, of the Weizmann Institute, Israel, began a similar appointment as a Visiting Chemist.

T.W. Gilbert, who spent the previous academic year with the Analytical Chemistry Research Group on sabbatical leave from the University of Cincinnati, returned for an additional three months of collaboration with the same group.

S.W. Feldberg returned from the University of Kansas where he taught for a semester on leave from Brookhaven.

G. Meinken returned to the Analytical Chemistry Service Group after completing a two-year, all-expense AEC-funded scholarship which enabled him to receive a BS degree from Rensselaer Polytechnic Institute.

L.G. Stang, Jr., continued as Editor of *Nuclear Applications*, a monthly journal of the American Nuclear Society, which is now in its fourth year of publication and which, because of the increasing number of papers contributed, went from one volume to two volumes per year.

C. Auerbach continued as Editor of *Chemical Instrumentation*, a quarterly journal published by M. Dekker, with the first issue appearing in 1968.

J.R. Weeks organized and chaired the discussion on sodium corrosion of fast reactor materials for the Libby-Cockcroft information exchange on reactor corrosion, held at Battelle Memorial Institute, Columbus, Ohio, in May 1968.

J.R. Weeks was invited to prepare a keynote discussion on Materials Behavior in Fast Reactors at the 9th INCO Power Conference in Wrightsville Beach, N.C., in May 1968, and again at a Polytechnic Institute of Brooklyn 2-day seminar on Material Considerations in Nuclear Power Plant Applications in New York City, October 1968.

J.R. Weeks served as a consultant to the Aerojet-General SNAP-8 project in January 1968, and spent four days in September 1968 in discussions with AECL personnel on materials compatibility problems with the Pb-Bi target-coolant of the Intense Neutron Generator. He presented a seminar on Corrosion in Liquid Metal Systems at Chalk River on September 27, 1968.

A.H. Fleitman and J.R. Weeks wrote Chapter 46, entitled Mercury, of the 3rd Edition of the *Reactor Materials Handbook*, and J.R. Weeks wrote Chapter 47, entitled Bi, Pb, Sn, and Their Alloys. D.H. Gurinsky was a section editor on Thorium and Thorium Alloys for the *Reactor Materials Handbook*.

Brookhaven, represented by T. Prach, was one of five laboratories which participated in a "round robin" conducted by the ASTM Oxygen in Sodium Task Force. The purpose of the "round robin" was to evaluate the mercury amalgamation analytical method for determining oxygen in sodium metal.

J.G.Y. Chow presented BNL's results at the 3rd Libby-Cockcroft Exchange Meeting on Effect of Irradiation on Structural Materials in Richland, Washington, June 1968.

D.H. Gurinsky spent July and August as a resident consultant at Gulf General Atomic in La Jolla, California.

J.M. Galligan spent the summer of 1968 as a guest scientist at the Max Planck Institut für Physik at the Technische Hochschule in Stuttgart, W. Germany. While in Europe, he presented a paper at the International Conference on Vacancies and Interstitials in Julich, W. Germany, September 1968, and an invited seminar at Euratom, Ispra, Italy.

J.M. Galligan was invited to present a seminar at Aerospace Corp., El Segundo, California.

D.G. Schweitzer was invited to write a book on thermodynamics to be published by the North Holland Publishing Co.

J.R. Weeks presented an invited discussion, entitled Estimation of Impurity Levels in LMFBR From Solubility Data, and Comparison With Impurity Behavior in Loops, for the International Conference on Sodium Technology and Large Fast Reactor Design, ANL, November 1968.

J.M. Hendrie became a Fellow of the American Nuclear Society on June 11, 1968.

The Heat Transfer Group of the Engineering Division has continued publication of the *High-Temperature Liquid-Metal Technology Review* for the sixth year.

In the summer of 1968, C. Hsu of the Heat Transfer Group was invited to lecture at the Summer Science Seminar held at National Taiwan University in Formosa. He gave a series of lectures, entitled Mathematical Methods in Heat Transfer and Continuum Fluid Mechanics, to a group of engineering faculties and graduate students.

F.L. Horn and A.W. Castleman, Jr., were the US representatives at the IAEA Symposium held at the United Nations in August 1968 to discuss operating and developmental experience in the treatment of airborne radioactive wastes. Their paper was entitled $\text{Pu}_2\text{O}-\text{UO}_2\text{-Na}$ Aerosols Produced by Vaporization of Fast Reactor Core Materials.

T.V. Sheehan served as Program Chairman for the ASME Nuclear Engineering Division at the Winter Annual Meeting held in New York City, December 1-5, 1968.

D.W. Huszagh spent two weeks in Buenos Aires, Argentina, for the IAEA and BNL to inspect the site of the Brookhaven Portable Cesium Irradiator to be installed in the early spring of 1969.

R.D. Baldwin, Jr., presented a paper and was Vice Chairman for a Performance Test Codes Session at the ASME Winter Annual Meeting in New York City, December 1-5, 1968.

Reactor Physics Division

(04-40-01-02-1, 04-60-70-01-1)

The research of the Theoretical Reactor Physics Group has been concentrated in areas that are leading to better understanding of fast reactors. The work has involved the study of problems in

the theory of asymptotic experiments in fast systems, reactor kinetics, fluid dynamics, and mathematical methods with particular emphasis on application to the calculation of resonance absorption. Some work on neutron thermalization continued in order to bring the research to logical conclusions and to provide guides for the solution of transient problems in fast systems.

There has been initiated a study of the response of subcritical fast reactors to pulsed neutron sources. In the course of this work an explicit expression for the slowing down Green's function has been obtained. Attention has been focused on the situation for which the system is so subcritical that the fundamental decay constant seems to "disappear into the continuum." By an analytic continuation of the "dispersion law" it has been shown that the pole bifurcates (or N-furcates) and appears on an adjacent Riemann sheet, and this explains the near exponential behavior that occurs experimentally.

In nonlinear space independent reactor kinetics, a perturbation method for estimation of permissible bounds on initial disturbance was developed. It was shown that the bounds predicted by other techniques are overly restrictive and can be relaxed for a wide class of reactors. The effect of delayed neutrons on point reactor kinetics was studied, and it was found that the delayed neutrons often control the character of power oscillation. Methods for improving the prompt jump approximation by means of an expansion in a small parameter were developed, and it was shown that significant improvements in calculational technique can be achieved. Space dependent kinetics have been studied by means of an iteration procedure and by modal expansions. For the Fuchs-Nordheim model the iterative procedures were shown to have a wider range of validity than the modal expansion method.

Confirmation of a crucial condensing length in two-phase condensing flow has been obtained. This has made it possible to correlate stability data in terms of the parameters used to define the steady-state condensing length. The work on the numerical solution of the Navier-Stokes equation is being directed toward problems that arise in the safety of sodium-cooled reactors.

Developments in mathematical methods have shown that the use of iterative solutions with trial operators provide an improvement over the usual variational calculations for resonance absorption.

Reactor analysis work includes progress in methods and code development, analysis of fast and intermediate critical experiments, and work directed toward testing ENDF/B cross-section data.

Analysis of epithermal Pu-Al-D₂O lattice experiments has involved producing computer routines and cross-section libraries, as well as carrying out some of the necessary fundamental mode and Monte Carlo studies. Information on the high energy cross section of Pu²³⁹ will come from this analysis, as well as the analysis of boron-covered foil activations in the HFBR and the analysis which is under way of fast reactor critical experiments.

Methods development includes additions to the NOMURK reactor dynamics code systems. These additions cover space-time and multi-temperature treatments in subcodes that include xenon effects, one-dimensional time studies, and a restricted two-dimensional treatment. The method of overlapping groups has been applied to a transport theory study of criticality and activation rates in multiregion reactors. Progress has been made on programming a Monte Carlo resonance capture code which will be applied to analysis of thermal reactor criticals to test ENDF/B cross sections as well as to fast reactor calculations.

Studies undertaken for the Division of Reactor Licensing include work on reactor power distributions and reactivity effects. Measurement and detection of power shape in a pressurized water reactor core by instruments outside the pressure vessel were examined by means of a Green's function technique. This yields a sensitivity function which can be combined with an arbitrary power distribution to give the detector response to the power distribution. The effect on the power distribution of a localized control rod perturbation was studied.

Methods and cross-section data were tested by calculating moderator coefficients for comparison with experimental results reported for zero-power experiments containing dissolved boron. The effect on the coefficient of control rods that were present in the experiment is being studied.

Reactivity effects of fuel motion simulating bowing were calculated over a range of inward and outward movements. Calculational methods for obtaining control rod worth have been studied and tested for use in subsequent calculations.

The Experimental Reactor Physics Group completed and analyzed measurements of the produc-

tion of Cf²⁵⁴ in the HFBR by successive capture of two neutrons in Cf²⁵². The production of Cf²⁵⁴ by epithermal neutrons was found to be considerably less than had been predicted on the basis of systematics in neutron cross sections. However, the inferred value of absorption resonance integral of Cf²⁵² is consistent with a subsequently published value.

The fast critical assembly known as FS-1 was brought critical and is currently being used to study heterogeneity effects in fast reactors and as a neutron source for the development of a fast neutron spectrometer. Electronic and computer routines have been completed for γ -ray subtraction by pulse shape discrimination, and preliminary neutron spectra in FS-1 have been obtained.

A format for compilation of fast reactor experiments was developed and has been reviewed by the European-American Committee on Reactor Physics, the Atomic Energy Commission, and various laboratories engaged in fast reactor experiments. The work of evaluating and compiling significant experimental information that may be used in testing analytical methods and cross sections is now under way.

A flying spot digitizer was adapted to count fission tracks in thin plastic foils. Standard conditions for etching, photographing, and scanning were developed to obtain reproducible results. The technique has been used to measure fission rates in exponential assemblies and for absolute power calibrations in critical assemblies.

Preliminary work on the measurement of delayed neutron parameters proceeded with the development of tapes used to transport the fissionable material and the development of detector systems. Sample tapes are currently undergoing tests to determine tape endurance and fuel loading techniques. A neutron detector system with an almost flat energy response was constructed according to a design developed at Los Alamos.

Analysis of the BNL U²³⁵-graphite critical experiments was completed using the conventional B_1 approximation and also the moments method using Monte Carlo calculations. In addition, a technique for analysis of small reflected assemblies was completed. This method is based on the DSN code ANISN and it corrects the tendency of diffusion theory to underestimate the reactivity.

A preliminary series of six lattices composed of Pu-Al rods in D₂O were conducted for the purpose of verifying the neutron capture-to-fission ratio in

plutonium in the epithermal energy range. As a result of the preliminary series of measurements, experimental and analytical methods were developed and improved for the final series now in progress.

Nuclear Materials Division

(02-40-01-00-0)

The Nuclear Materials Division was formed this year. This Division acts as a Technical Support Organization (TSO) for the USAEC's Office of Safeguards and Materials Management (OSMM). The function of the group is to provide technical advice and guidance to the OSMM in a number of areas related to research and development in safeguards.

A simple version of the "strategic point" concept, an approach for safeguarding nuclear facilities, has been studied to provide a basis for comparison with the material balance concept currently employed in the United States. Similarities and differences are being clarified to compare such factors as cost effectiveness, credibility, and political acceptability.

On the basis of visits and discussions with OSMM contractors and other institutions with similar interests and upon an evaluation of the status of U.S. instrumentation and data handling, recommendations have been prepared for conducting future research and development. The TSO has also reviewed a number of proposals for research and development received by the OSMM. Analysis of the current research program has suggested that proposals for research in some apparently neglected areas might be solicited.

In conjunction with the need for development of new techniques for inventory measurement, a survey was made to categorize the type and form of special nuclear materials that are being processed in industry. The survey included visits to typical nuclear facilities, and an informal report was submitted to OSMM.

Scintillation detectors and analyzers now used by the U.S. and IAEA inspectors were evaluated. In cooperation with the Arms Control and Disarmament Agency, several portable passive analysis instruments are being procured for field tests. Techniques in high resolution γ ray spectroscopy and passive neutron measurements that might be applied to safeguards have been reviewed.

The program on seals as safeguards tools is being conducted in two parts: the testing of seals and the analysis of their use. IAEA and Internal Revenue Service seals are being tested to determine their effectiveness under present IAEA procedures. A system-oriented analysis of sealing operations has started in order to identify the applicability and limitation of seals as compared with alarm devices and attack-resistant volumes.

Information is being collected on the present U.S. safeguards system in order to relate the research and development program to current needs. Systems studies under way at the National Bureau of Standards and at Battelle-Northwest Laboratory will also contribute to this objective. TSO will use these studies to identify the sensitive points in the nuclear fuel cycle to determine where research and development deserves special emphasis.

A report giving an estimate of IAEA costs and manpower requirements under the Nonproliferation Treaty was prepared for the OSMM for presentation to the U.S. Senate Foreign Relations Committee. Forecasts were made for the period 1970-1990.

A glossary of special terms used in safeguards is being assembled. This information is being stored on IBM cards to permit sorting and classification.

National Neutron Cross Section Center

(04-40-01-03-1, 05-03-01-03-0)

An Advisory Committee was appointed by the Nuclear Engineering Department to review the activities and discuss objectives of the National Neutron Cross Section Center.

Efforts to detail the "content" of a new experimental data storage and retrieval system (SCISRS II) began, and assistance was obtained from various experimental and evaluation groups as to what information and format would render this library an invaluable tool to all users.

The first version of the ENDF/B library was distributed to cross section users in the United States, Canada, and ENEA member countries. This library was the result of a cooperative program among US AEC-supported laboratories to increase the number of completed data sets available to reactor designers.

Various computer programs pertaining to the processing aspects of the ENDF/B library were extended not only to improve their versatility and operating performance, but also to include the data in the newly proposed photon files.

An elemental version of the SCISRS II system was developed, the format of which was designed to accommodate a wide variety of data as well as to allow for the separate storage of bibliographic and numerical information. Moreover, studies are continuing on ways to automate the compilation of angular distribution data so that plots and curves can be reproduced with a minimum of human interaction.

A systematic procedure for estimating the nuclear properties of transuranium isotopes was completed. This analysis provided a method for determining the thermal values of the fission and capture cross sections, fission and capture resonance integrals, average number of prompt neutrons, and the average kinetic energy of the fission fragments.

An optical model study was completed of total cross sections and elastic angular distributions for Pb^{208} , Pb^{207} , Pb^{206} , and Bi^{209} . Good fits of the parameters to the experimental data were found at 1.0 and 2.5 MeV.

Optical model calculations were carried out for Co^{59} from 0.1 to 4 MeV, and for Cf^{252} from 1 keV to 15 MeV.

The coupled channel code JUPITER I was modified to generate transmission coefficients corresponding to both spherical and nonspherical potentials.

A study of the resolved resonance region of Co^{59} was initiated, and a similar study of Ho^{165} was completed.

A program, SIGPLOT, was written for calculating single-level cross sections, with an option for multi-level scattering effects, from resolved resonance region parameters stored on ENDF/B tapes. A program, AVERAGE, was written for calculating average cross sections in the 1 to 100-keV region. In addition, a program, SIGTEST, based on the Adler-Adler formalism, was written and tested.

Formats were set up for storing Reich-Moore and Adler-Adler multilevel resonance parameters on ENDF/B tapes. The multilevel programs COMBCO and CODILL are being evaluated.

New insights into the statistical theory of nuclear reactions were gained through use of the recently introduced random matrix ensembles. In particular, it has been possible to apply this

method to cross section fluctuations, polarized nuclear reactions, and influences of time reversal noninvariance on nuclear reactions.

Evaluation and Technical Assistance Group

(04-01-91-01-1)

The Evaluation and Technical Assistance Group continued to assist the AEC in program reviews and the evaluation of specific areas of interest. BNL personnel participated in the study of the U.S. nuclear power industry for the Reactor Development and Technology Division of the AEC. BNL personnel constituted the working group of the thorium systems task force which evaluated the technical and economic potential of the molten salt breeder reactor, and also assessed the role of thorium in the U.S. civilian nuclear power economy. The results of these two studies were submitted to the AEC in two reports, the latter of which was circulated by the AEC to interested groups in industry and the national laboratories for comments prior to its formal issuance.

BNL personnel also served on the advanced converter reactors and systems analysis task forces. The final advanced converter draft report was reviewed and comments were submitted to the AEC. BNL personnel served as members of the Research and Development Committee as well as a special working group to help in writing the final systems analysis report. Assistance was rendered in writing several sections of the final report, in evaluating the linear program output, and in devising ways of presenting the data, which included the preparation of >100 graphs encompassing each reactor case investigated.

The remaining three (of ten) program plans for the Liquid Metal Fast Breeder Reactor Program Office were reviewed at the request of the Reactor Development and Technology Division; these were sections on over-all plan, plant design, and fuels and materials.

BNL is participating in the development of codes and standards applicable to the reactor field, as part of an AEC-sponsored program at ORNL and AI for the water reactor and LMFBR programs, respectively. Detailed comments on some 52 standards have been submitted thus far. BNL is also represented on subcommittees of the US-ASI-NSB Standards Committee N101.

Chemistry Division

(05-05-03-00-0)

Improvements have been made in the procedures used in studying the electrical double layer that forms at electrode-electrolyte interfaces in liquid metal-fused salt systems. The dependence of capacitance on potential was determined for dropping bismuth and dropping lead electrodes in LiCl-KCl eutectic. As potential increased, the capacitance went through a minimum. Varying the temperature had very little effect on capacitance.

An experimental technique that had never previously been applied to fused salts, the scattering of cold neutrons, was perfected and data were obtained on molten zinc chloride, potassium chloride, and certain mixtures of the two. The technique, which is a form of spectroscopy, gives information that is of value in testing theories of the structure and dynamics of fused salts. It should help, for example, in providing criteria of the existence of certain much-disputed complex ions in such systems.

Cathodic chronopotentiograms were obtained on chlorine dissolved in several fused chlorides. From the results, together with previously measured solubilities, it was possible to determine diffusion coefficients of dissolved chlorine. In a new series, the solubilities of bromine gas in fused bromides were measured. For these systems the temperature coefficient of solubility is negative, unlike that of chlorine in chlorides.

The effects of temperature on the radiolysis of perfluorobiphenyl, a very stable fluorocarbon, and of perfluorobicyclohexyl, a relatively unstable one, were determined more precisely. For the first, it was possible to derive an apparent activation energy of 0.5 kcal/mole for the radiolytic decomposition process. With the latter, the temperature coefficient of purely thermal decomposition was much greater than that of radiolysis, and a similar calculation could not be made.

The formation of valence isomers in the irradiations of aromatic fluorocarbons has been put on a more quantitative basis. The perfluoro analogs of Dewar benzene and xylene are formed from the Kekule forms with G -values of 0.02 and 0.05 molecules/100 eV, while Dewar benzene itself reverts under irradiation to the Kekule form with $G=20$.

Radical ions were prepared from a number of substituted porphyrins by electrolytic oxidation,

as a step in the study of their oxidation-reduction behavior; it is, of course, because of their oxidation-reduction chemistry that porphyrins are key compounds in respiration and photosynthesis. Spectroscopic measurements, both optical and esr, were made on the radical ions produced and structural information was derived therefrom.

The rate of vaporization of graphite was measured in the range 2400° to 3400° K, higher than ever before. From the results, the heat of vaporization was deduced to be 210 ± 10 kcal/mole of vapor. This is consistent with the postulation of C_2 as the evaporating species. Confirmation for a value around 200 was obtained from experiments in which sample weight loss was compared with the electrical energy put in (after corrections for various losses), and from spectroscopic data.

Two new phenomena in graphite pyrochemistry were discovered. When material evaporating from incandescent graphite at 3000° to 3300° K is condensed on a glass surface at liquid N_2 temperature, it retains stored energy; this becomes evident when flashes of light are emitted after warming the glass surface. Also, graphite surfaces in this temperature range become surrounded by a partially opaque cloud of microscopic carbon particles. This can cause a photoelectric pyrometer to read too low.

The reaction of hydrogen with a large number of alloys was investigated and many were found to take up the gas reversibly. Thermodynamic data were obtained for several of the systems. Two of the most interesting hydrides were those formed by the intermetallic compound FeTi, namely, FeTiH and FeTiH_{1.8}, and the higher hydride of vanadium, VH₂. In all these cases, The decomposition pressure was appreciably >1 atm at room temperature.

Radiation Division

(04-40-04-03-1, 05-05-03-00-0, 08-03-02-00-0,
08-04-01-00-0, 08-05-00-00-0)

The work in radiation chemistry has been concerned primarily with determining the mechanisms of reactions induced by radiation in organic solids and liquids and in simple inorganic compounds. Studies were also started on the properties of synthetic membranes, including the preparation of membranes by both conventional and radiation-polymerization techniques.

The study of the reactions of several irradiated amides with oxygen, nitric oxide, and sulfur dioxide has demonstrated that the reaction rate is diffusion-controlled. It was also shown that the sulfur dioxide molecule is too large to diffuse between the crystal layers, and so it reacts mainly with radicals on surfaces and trapped in defects. The work on isomeric effects in the radiolysis of substituted aromatic compounds was extended to the nitrophenols and the fluoronitrobenzenes. The molecular weight distribution in polymerized styrene produced from exhaustively dried styrene is being compared with that of material produced from the normally dried monomer, over wide temperature and dose-rate ranges. Also under study is the temperature dependence of the polymerization rate of very dry α -methylstyrene over a range of dose rates. The irradiation of nitrous oxide in the solid, liquid, and gaseous states showed a remarkable constancy in the G -value for nitrogen production. Work has continued on the radiolysis of liquid ammonia and of nitrous oxide absorbed on molecular sieves.

The goal of irradiation processing is the large-scale production of industrial chemicals by the use of nuclear energy, utilizing both fission and isotope sources. In the Chemonuclear Program, the Chemonuclear In-Pile Research Loop in the BGRR has been completed and the first run made. This was an unfueled dosimetry run made to establish the neutron and gamma backgrounds along the in-pile section. The loop met the design specifications and presented no difficulties in operation. Modifications on both gas-bearing compressors were completed and both are operational. The capsule studies on the irradiation of N_2 - O_2 mixtures with Co^{60} γ , pile radiation, and fission fragments at 5 and 68 atm have been completed. Once-through homogeneous N_2 - O_2 flow experiments in a Co^{60} γ field were started. Further experiments have been carried on with two-phase water and N_2 - O_2 systems in a γ field, using both bubble and spray columns. A study of ozone synthesis from oxygen at low temperatures in a γ field was begun. Results showed increasing G -values down to $-100^\circ F$, the lowest temperature reached. It was found that the addition of a few percent of N_2 to the O_2 increased the G -value by a factor of 3. This reaction will be studied in the chemonuclear loop.

Although there has been no experimental work done this past year on the radiation polymeriza-

tion of ethylene and the production of copolymers, the high level of industrial interest has resulted in numerous requests for information and advice. The joint program with the U.S. Bureau of Reclamation on concrete-polymer materials has continued at a high level, with striking improvements resulting in many properties of concrete, including both compressive and tensile strength, moduli of elasticity, rupture, and flexural elasticity, resistance to freeze-thaw, water permeability, water absorption, and corrosion resistance to distilled water and to sulfate brines. The decomposition of CO_2 , the fixation of nitrogen, the production of ozone, and the decomposition of iron pentacarbonyl in the presence of solid materials is being studied in the program on the radiation chemistry of heterogeneous systems. The program on the effect of γ and β radiation on electrode reactions is continuing.

Work both theoretical and experimental has continued on the analysis of radiation chemical reactors. This work is concerned with developing methods of designing and scaling up chemical reactors for radiation processes and the understanding of the kinetics of radiation chemical reactions. Theoretical studies include the effect of mixing and diffusion upon reactor performance, the characteristics of continuous stirred-tank reactors when used for radiation-induced polymerizations, and the consideration of the thermal stability of a photoinitiated chain reaction. An experimental tubular radiation chemical reactor containing a 20 Ci Sr^{90} - Y^{90} source has been operated, using a chemical dosimeter solution as reactant to measure conversion as a function of mean residence flow under both laminar and turbulent flow conditions. The dose rate distribution and the mean absorbed dose rate were determined for a prototype Sr^{90} extracorporeal blood irradiator. Several runs were made with a radiation chemical reactor using Co^{60} as the radiation source and Fricke dosimetry solution as the reactant, measuring conversion as a function of reactant flow rate, stirrer speed, and source strength. Experiments were continued on the rate of photopolymerization in a partially illuminated, agitated vessel as a function of stirrer speed. A new type of dosimeter for measurements in the range of 5 to 50 krad has been developed, employing radiation-sensitized quartz plates.

Radiation engineering is concerned with the development and utilization of radiation sources for

practical purposes. The source inventory at the HIRDL was increased by additions of Co^{60} , Cs^{137} , and Sr^{90} . The usage of the hot cells continued at near capacity rates. The new underwater γ facility at the HIRDL has been completed. It provides dose rates from 5×10^3 to 10^7 rads/hr. The package conveyor system for the continuous processing of large quantities of food and other materials was redesigned and rebuilt for more efficient operation and greater capacity. Efforts continued on the development and modification of computer codes for predicting γ and β dose distribution. The development of Co^{60} , Cs^{137} , and Sr^{90} sources also continued, as did work with dosimeters and dose-distribution measurements. The Shipboard Irradiator and the BPC Irradiator were redesigned and rebuilt to conform to Department of Transportation requirements. The Portable Cesium Irradiator is being redesigned. Installation and maintenance operations were supervised for several irradiators located in the United States and abroad.

The feasibility of the isotope ratio tracer method for following sulfur compounds in the atmosphere was demonstrated under the Atmospheric Sulfur Pollutants Program and a working technique developed. Field studies are under way in New Haven, New York City, and in western Pennsylvania. This is a cooperative program with the U.S. Public Health Service, and involves the Analytical Chemistry Group of the Hot Laboratory Division and the Meteorology Division of the Instrumentation and Health Physics Department.

Other areas in which progress is reported include the plasma betatron accelerator, the structure of ball lightning, time-dependent transport calculations, a new hybrid fossil fuel-nuclear energy MHD cycle, and the study of electron recombination after pulsed radiolysis at pressures in the region of 100 to 1000 torr.

Hot Laboratory Division

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

The research work of the Hot Laboratory Division comprises three main fields: nuclear and radiochemistry of special isotopes, analytical and physical chemistry, and medical radionuclide applications. In addition, some service work is provided in the form of radiography, waste treatment, chemical analysis, special isotope production, and laboratory operation.

Nuclear and radiochemical research problems included studies of the chemical behavior of excited atoms and studies of nuclear reactions. Progress in the first area included discovery of a remarkable and unexpected difference in the chemical behavior of two similar zirconium and hafnium compounds. Differences observed between the neutron-induced activity of metallocenes and that of phthalocyanines were explained by considerations of molecular structure. An unexpected but very real isotope effect observed in the behavior of hafnocene under neutron irradiation suggested the existence of unknown isomers of certain hafnium isotopes. Progress in the study of nuclear reactions included establishing a value of 21 ± 11 b for the capture resonance integral for Cf^{253} and corroborating certain other recently reported cross sections for transplutonic nuclide formation. A systematic determination of individual cross sections was begun in an effort to provide necessary information for optimizing the production of isotopes of mass ≥ 252 . In the study of ternary fission, evidence continues to be gathered indicating that the triple coincidence events being measured are indeed due to ternary fission rather than to scattering and supporting the dominant role of underlying shell structure in determining the three-way nuclear cleavage. A related experiment established 10^{-10} atoms as the upper limit for the yield of Si^{32} per unit fission of U^{235} . Extensive calculations of level densities of excited nuclei have shown that the densities for states of positive parity are nearly the same as those for states of negative parity, with certain notable exceptions when the ratio of numbers of single-particle levels for one parity relative to the other exceeds eight. Extension of a previous study of nuclear evaporation processes into a region of the periodic table in which charged-particle (rather than α -particle) emission is expected to dominate indicates that the limits on the production cross section of highly neutron deficient nuclides vary greatly between different regions of the periodic table and even between adjacent nuclides.

Analytical and physical chemistry research problems included studies of mixed-metal complexes and of the dimerization of certain organic radicals. Progress in the complex study included work that showed that hydroxy bridging is not involved in mixed-metal complexes, even though the hydroxy group seems to be necessary for the formation of the complex. A very strong indium

uranyl citrate complex was discovered; the fact that it forms more readily than the dimer of uranyl citrate indicates the importance of considering it when analytical techniques involving extraction from aqueous citrate media are being devised. Chronoamperometry was used to study the rate of dimerization of several substituted triphenylamine cations. A digital computer was used to simulate hydrodynamic-diffusion-kinetic processes occurring at rotating disc electrodes.

Progress in the development of medical radio-nuclides included a method for making very high specific activity (>1 Ci/g) Mg^{28} that also has extremely high radiopurity ($<0.001\%$ radiocontamination). A low-cost, high-yield, high-purity method of making Tc^{99m} widely available was developed. Gel chromatography was found useful for studying the stability and behavior of compounds labeled with Tc^{99m} .

Metallurgy and Materials Science Division

(04-40-02-02-1, 04-40-02-03-1, 05-06-01-02-0)

The program of the Liquid Metal Center includes studies of the corrosion behavior at 760° to 815°C in sodium of materials for the LMFBR program, the mechanism of corrosion of materials in liquid sodium, and the chemistry of liquid sodium solutions.

Thermal convection loops continue to be used to study the behavior of a wide range of possible fuel-cladding materials in sodium. Oxygen activity is controlled by one or more of the following techniques: cold-trapping, Zr hot-trapping, and Mg- or Li-gettering. Carbon activity is varied by using both types 321 and 316 SS as loop piping. In the alloys tested, the corrosion rate increases with the Ni + Cr content of the alloy; the Co-base alloy S-1 corrodes the least, followed by stainless steel and IN-800, which lost ≈ 4 times the weight lost by S-1. The temperature dependence of the corrosion rates of all three alloys is the same between 700° and 760°C .

Co-base alloys are being studied as potential high-temperature fuel-cladding materials for an LMFBR because of their increased strength at 750°C . A series of new alloys is being developed containing 2 to 3% Ti which have mechanical properties at 800°C comparable with those of the stainless steels at 650°C .

Forced circulation loop tests have shown that the corrosion rates of the Co-base alloys HA-25 and UMCO-51 are much less affected by an increase in the oxygen level from 4 to 12 ppm than are the corrosion rates of stainless steels. X-ray fluorescence and metallographic observations suggest deposition of iron occurs on the surface of the Co-base alloy specimens when the oxygen level in the Na is 12 ppm but not when it is 4 ppm. A comparison of the BNL corrosion data on the stainless steels with those from the UK, RML, and GEAP shows good agreement at comparable oxygen levels and velocities.

The corrosion of refractory metal alloys is being studied in a forced circulation loop with both hot and cold trap capabilities for controlling oxygen. A 2000-hr test was completed under Zr-hot-trapped conditions (<1 ppm oxygen) in which the V- and Nb-base alloys all gained weight at a rate that leveled off at ≈ 0.5 mg/cm²-mo for 3 V-base alloys and ≈ 0.15 mg/cm²-mo for Nb-1 Zr. The rate of weight gain was nearly independent of temperature between 700° and 760°C . Specimens of the Mo-base alloy TZM did not change in weight. After the oxygen level was raised to ≈ 4 ppm, all the V- and Nb-base alloys lost weight, but the Mo-TZM alloy was unaffected. The 321 SS specimens corroded at a rate comparable with the results obtained in FCL-1 at the same oxygen level.

Construction was completed of a loop to test high-flux heaters. Heat fluxes up to 10^6 Btu/hr-ft² were reached at a Na temperature of $\approx 600^\circ\text{C}$ using a NaK-cooled 50-kW, 10-kHz induction heater. The specimen holder in the heater area is a Permendur recepter. A long-term run has been started in which the maximum specimen temperature is $\approx 650^\circ\text{C}$ and the heat flux is 10^6 Btu/hr-ft².

The solubility of Ni in Na has been shown to range from ≈ 0.6 ppm at 450°C to ≈ 1.4 ppm at 600°C . The solubility of Fe in Na has been shown to be ≈ 0.3 ppm at 486°C and ≈ 0.85 ppm at 550°C . It appears to be independent of oxygen in the Na below an oxygen activity of ≈ 0.2 times its solubility. The apparent Fe solubility increases with the oxygen activities in Na above this value. Combination of the present low-oxygen results with other recent determinations at higher temperatures yields a tentative solubility equation for Fe in Na.

The chemical activity of oxygen in Na held in a stainless steel system is found to be buffered by

one or more substances present in or on the stainless steel surface. Further experiments in an oxidized Zr beaker containing 2 g of a mixture of Cr and Cr_2O_3 powders confirmed that Cr is the probable buffering agent, and that, at 500°C , the buffered activity in the presence of Cr and Cr_2O_3 powders corresponds to that of a Na-17 ppm oxygen binary solution.

For this work, the Cu-Cu₂O reference electrodes in the commercial electrochemical oxygen meters are replaced by a Na-Na₂O reference electrode, in which there is always excess solid Na₂O present. The measured potentials of this electrode against Na containing known amounts of oxygen yielded an equation for the solubility of oxygen in Na. There is an apparent inflection in the potential-temperature curve at 315°C which is believed to reflect a phase change in solid Na₂O at this temperature.

Work is complete on studies of the reaction of HCl with Na and Na-Ba solutions. The reaction occurs in two stages: the first produces H₂ and NaCl or BaCl₂ and is controlled by processes of a physical nature; the second is the reaction of Na with the H₂ produced.

There is an interaction of hydrogen and oxygen in liquid Na at 400°C that reduces the oxygen activity at constant oxygen concentration, as observed by following the electrochemical potential of oxygen during a reaction of the Na with H₂ gas. The reaction of CO with Na at 200°C occurs in three stages: an induction period in which a film forms on the Na, a rapid absorption stage in which the metal surface appears to be clear, and a second stage of negligible reaction rate in which the surface remains apparently clean.

Construction of the Na chemistry loop was completed in 1968. It is currently undergoing shake-down runs.

The electrical conductivity of UNC ThO₂-Y₂O₃ meter tubes was determined over a range of oxygen pressures from air to very dry hydrogen and at temperatures from 200° to 800°C . The predominant conduction mechanism was concluded to be ionic in the oxygen pressure range from air to 10^{-30} atm at temperatures from 300° to 850°C . To extend the measurements to oxygen pressures corresponding to <1 ppm in Na, studies with Si-SiO₂ are being made.

Tests of the commercial Cu, Cu₂O reference electrode in the UNC oxygen meter suggest that potentials closer to theoretical can be obtained if

the operating temperature of the meter is raised from the recommended value of 320° to 350°C . Once the reference electrode is contaminated with air, it does not recover theoretical potentials.

The use of electrochemical oxygen meter electrodes is being studied as a means of making coulometric additions or subtraction of oxygen to or from sodium. No net transfer of oxygen through ThO₂·Y₂O₃ from saturated to unsaturated solutions of oxygen in Na was observed at 500°C and 0.1 to 5 mA of current, possibly because the applied voltage caused the electrolyte to become an electronic conductor.

An electrochemical carbon meter is being studied; CaC₂ appears to be a suitable electrolyte reversible to carbon. The emf developed by the experimental cell, graphite||CaC₂||Zr, ZrC, was within 10% of the theoretical value between 250° and 400°C .

Contributions of stainless steel tube surfaces to the oxygen analyzed by the amalgamation method were found to range from 1 to 2 μg per linear inch of $\frac{1}{2}$ -in.-o.d. tubing. This problem arises when loop bypass samples are analyzed without extrusion of the Na. The U-gettering method for O in Na has been shown to be applicable up to 30 ppm O in Na at 500° . The gettering rate is proportional to the mass transfer coefficient of oxygen in Na.

When Co-base alloys are irradiated to 10^{20} , $E > 0.82$ MeV, the commercial alloys that have had the recommended heat treatment for high strength lose high temperature ductility in a manner similar to the stainless steels; however, these alloys are much stronger at 650°C than the stainless steels. Refining the grain structure of these alloys by additions of Ti or by thermal-mechanical treatment produces improved high temperature ductility after irradiation.

Thermal-mechanical treatments have also been shown to improve the ductility of stainless steels after irradiation, presumably because they alter and refine the grain size. Special steels with $<0.01\%$ N+C also retain 3 to 4 times the ductility of commercial stainless steels at 650° and 750°C after irradiation. Superplastic Fe-Cr-Ni alloys are ductile at 650°C after irradiation, and remain superplastic at 750°C . The increases in post-irradiation ductilities of the Fe-Cr-Ni alloys were obtained in most cases without any sacrifice in strengths over commercial steels.

The lower limit below which irradiation does not affect the slip mechanism in Fe below 250°K

is $< 10^{18}$ nvt. Above 250°K , however, 10^{18} nvt irradiation has no effect on the slip mechanism. During stage IV recovery of cold-worked and neutron-irradiated Nb, both oxygen interstitials and self-interstitials migrate.

The temperature dependence of the critical resolved shear stress in W crystals was found to be markedly reduced by avoiding surface damage.

No effect of 2×10^{20} nvt was detected on the concentration of fine Fe_3C particles in Fe-0.03% C. No effect of irradiation was detected on the fracture mechanism at 77° and 298°K of Fe containing 0.11 and 0.35% C.

Effects of fast-neutron fluence on the ductile-to-brittle transition in Ferrovac E iron tested in slow tension are related to effects of fluence and temperature on the upper yield stress. Conflicting effects of fluence on the transitions in impact tests are related to effects of fluence and temperature on the strain-hardening rate.

The properties of hysteretic superconductors are shown to lie between two limiting types. One type exhibits isothermally reversible paths and retains fields of one polarity. The other type does not exhibit isothermally reversible paths, and can simultaneously retain fields of both polarities.

The diamagnetic and field retaining properties of thin-walled type I hollow cylinders can be changed by more than an order of magnitude through the introduction of surface strains. These effects can be explained by including surface and interface energy terms in the thermodynamic state function of a superconductor.

The dynamic behavior of superconductors in general contrasts with their static response to a constant magnetic field. A new theory is being developed to explain this effect. As predicted, conductivity increases were observed in the normal state as the material approaches the superconducting states because of statistical fluctuations of the normal state electrons into unstable superconducting states.

An attempt is being made to observe directly the ordering transition of nuclear spin system of solid ^3He , which is inferred by the present data to occur at a temperature of $\approx 0.002^\circ\text{K}$. Work is in progress to achieve temperatures in this range. The currently available techniques are believed to be adequate when the residual field gradients can be further reduced.

Extremely disordered films have been produced by deposition of metals onto cryogenic substrates.

The conditions under which maximum transition temperatures can be attained in these films have been studied. The conduction mechanism in near-monolayer films behaves like that in a semiconductor in the normal state; transition temperatures are also depressed.

The resistivity of liquid Hg alloys can be explained if the pseudopotential is assumed to be volume dependent. Measured volume changes on alloying are treated as if associated with the Hg component alone. Experimental data on the resistivity of Hg-In alloys can be satisfactorily explained with the Faber-Ziman theory using a hard sphere structure factor and a volume- and energy-dependent pseudopotential for the Hg.

Significant deviations are observed in the resistivity of Bi-Ga alloys at up to 8° above the consolute temperature, which are interpreted as due to concentration fluctuations.

In electromigration in liquid alloys, the direction of migration has been explained in terms of the difference in resistivities of solute and solvent. This behavior appears to break down for combinations of polyvalent and monovalent metals. Data on Na-K alloys show a "null point" at 34 at. % K, corresponding to the weak compound Na_2K , at which no separation of Na + K by electromigration is observed at temperatures below 170°C . Separation at higher temperatures is attributed to changes in the electron density of the alloy with temperatures.

The diffusion coefficients of Ag, Cd, In, and Sb in liquid Na were measured; all of them are less than Nachtrieb's value for self-diffusion in Na.

Computer calculations of the molecular dynamics of solid and liquid metals have been used to explain the observed increases in the superconducting transition temperatures of thin composite films. Calculations of the diffusion coefficients of mixtures of liquid metals have shown that the motion of a component with heavier mass than the solvent agrees with hard-sphere calculations, whereas motion of a component with lighter mass than the solvent is constrained by the surrounding solvent atoms.

In the area of service work for programs outside the department, the copper to carbon steel welds were examined for the AGS, the phases in a Ag-Hastelloy B-NbSn sandwich were identified for the magnet group, and poor joint penetration of solder was discovered in the braze joints for the AGS main ring.

Engineering Division

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

The work of the Heat Transfer Research Group continues to be devoted primarily to the study of forced-convection heat transfer to liquid metals. It includes liquid-phase and boiling flow, as well as analytical and experimental studies. In addition, there is a small effort directed toward exploratory investigations in other fields. In the past year, this has included a limited experimental study of high-temperature-gas heat transfer and a computation of physical properties of supercritical helium on the basis of theoretical considerations.

In the single-phase liquid-metal work, an experimental project was completed in which a study was made of the effect of rod displacement on heat transfer to mercury flowing in-line through an unbaffled rod bundle. The results of this study are relevant to the design of fuel element sub-assemblies and intermediate heat exchangers for liquid-metal-cooled reactors. It was found that displacement of a rod from its symmetrical position can result in a large reduction in its average heat transfer coefficient. This reduction increases exponentially with the amount of displacement. For a given direction and amount of displacement, the reduction is little affected by variations in cladding thickness and conductivity, but is considerably affected by flow rate. Not only does the displaced rod suffer a reduction in its own average heat transfer coefficient, but so do those *toward* which it is displaced. At the same time, the average coefficients of the rods *from* which it is displaced remain about the same. Thus, the over-all average coefficient of the group of affected rods decreases when a single rod is laterally displaced.

In the forced-convection boiling-potassium experiments, the emphasis continues to be centered on the problem of incipient-boiling superheat. It has been clearly demonstrated that the superheat depends, among other things, on (a) the pressure-temperature history of the system *prior* to boiling inception, and (b) the velocity of the heated stream at the *time* of boiling inception. In conjunction with the experimental work, analytical studies were carried out to extend the existing theory which governs the incipient-boiling superheat phenomenon. A facility is being built to extend this type of study to sodium. The results from such studies are pertinent to the operation of both

sodium-cooled reactors and liquid-metal boilers in Rankine power systems.

As an important part of the liquid-metal heat transfer research program, a probe for detecting and measuring vapor voids in two-phase liquid-metal flow and a special high-flux induction heater were successfully developed.

During the year, analytical studies were carried out on the following problems: (a) heat transfer to liquid metals flowing turbulently in the entrance regions of annuli, with emphasis placed on the effect of axial variation in the heat flux at the inner wall, (b) effect of axial conduction on heat transfer to liquid metals flowing laminarily in the entrance regions of annuli, (c) effect of rod displacement on heat transfer to liquid metals flowing in-line through unbaffled rod bundles, and (d) heat transfer to liquid metals flowing through closely packed rod bundles, with emphasis on the effects of cladding thickness and thermal conductivities.

A number of extended runs on the phosphate glass pilot plant at BNL were carried out over the past year, mainly to determine the range of dependable operating conditions for processing simulated wastes from projected high burnup fuels, and to develop improved mechanical designs and performance capabilities of the process units. Successful operation was obtained with a variety of Purex type wastes, including those derived from uranium burnup levels as high as 45,000 MWd/tonne of uranium. In a number of cases abnormal overload conditions were imposed to determine operating latitude for the major plant components, i.e., the evaporation-denitrator and the high temperature melter unit. Pilot plant operations have continued to provide basic information for the operation of the demonstration prototype plant with high-level radioactive wastes at Pacific Northwest Laboratories. An investigation of a number of new design schemes and equipment modifications was initiated during the year with the main objective of increasing the over-all capacity, or throughput, of the phosphate glass plant.

Development studies were continued on the processing of sulfate-rich melter off-gas condensates. Volatilization of the nitric and sulfuric acid fractions and retention of the potentially volatile fission products, notably ruthenium, for recycle to the phosphate glass appears to hold considerable promise as a practical and effective process step. Two methods of suppressing ruthenium volatilization have been investigated, i.e., low pressure and

reduced boiling temperature, and the use of reductants such as SO_2 .

The absorption of krypton and xenon on charcoal at temperatures in the range -275° to -250°C was found to be a very effective means of concentrating these gases from mixtures with nitrogen and air wherein the concentrations of Kr and Xe varied from 5 to 4000 ppm. Two discontinuous stages of operation with batchwise saturation and desorption are indicated. Desorption from the relatively small second stage would yield a gas mixture containing $>25\%$ Kr while producing an effluent concentration not exceeding 1 ppm.

The Safety Studies Program dealt entirely with the chemical problems related to the safety of sodium-cooled fast reactors. The general purpose of this work was to provide a fundamental understanding of the chemical and physical behavior of radioactive materials that are likely to be vaporized in the event of an accident.

Both analytical and experimental studies of the thermodynamic properties of fission product-sodium solutions continued. Partial molar excess free energies of mixing were deduced for NaI, Cs, Rb, Ba, Te, and Sb for the high concentration regions expected in the sodium thermal bond of high burnup fuel elements. Experimental measurements of the partial molar excess free energy of mixing of dilute solutions of sodium iodide in sodium were extended to temperatures well below the NaI melting point, yielding results that are consistent with those obtained at higher temperatures. Studies of the nonequilibrium vaporization of cesium from sodium were completed during the year. The results showed that the cesium release rate depended on diffusional resistances in both the liquid and gaseous phases. It was also shown that the Rayleigh equation for equilibrium vaporization is applicable for calculating the maximum extents of fission product release.

A study of the formation, agglomeration, and settling of PuO_2 , $\text{PuO}_2\text{-UO}_2$, and PuO_2 -sodium aerosols continued during the year. The airborne plutonium mass concentration of these aerosols was found to decrease at a very rapid rate initially. However, the rate of decrease dropped considerably after the first one to one and a half hours of settling time. The initial time dependence of the mass concentration is in quantitative agreement with an approximate theory that treats the settling of stirred, heterogeneous aerosols. The long-time behavior requires further study, but can be quali-

tatively explained. The presence of sodium has some effect on the time dependence of the airborne PuO_2 mass concentrations. This is attributed to the formation of larger but less dense particles.

The Engineering Assistance Group contributed $\approx 38,000$ hr to the support of departmental programs during 1968. 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, 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 reference designs of two alternative concepts and on supporting fuel development and experimental physics work. A primary goal of the current reference designs is to provide a basis for the evaluation of the alternative concepts as high-intensity neutron beam sources.

Alternative reactor shield zone and primary system arrangements are being considered in the reference design. A 60 vol % PuO_2 -Mo cermet fuel was selected for the pulsed reactor reference design; however, development work is continuing on other candidate fuels as backup materials for the pulsed reactor as well as for application to the alternative concept, an accelerator-injected pulsed reactor.

Fatigue testing of the cermet fuel, with the PuO_2 replaced by UO_2 , has been performed at two test frequencies. Mechanical fatigue tests were done at 186 cps and higher frequency tests (14,000 cps) were done by an ultrasonic technique. The test data agreed very well with the behavior predicted on the basis of the ultimate tensile strength of the material. Fuel development work was also performed on U-10 Mo alloy, U-Nb-Zr ternary alloys, and a U-Th dispersion.

An extensive series of critical experiments have been performed to provide for experimental evaluation of some of the techniques that have been proposed for optimizing the neutron pulse characteristics. The effects of poison liners and core cavities on the neutron lifetime and on the reactivity change associated with a moving reflector pulse block have been evaluated. Analytical techniques were developed to calculate these effects and the analytical predictions were compared with experimental values.

A series of beam source experiments was analyzed to provide a basis for the optimal design of the beam source moderator region.

NUCLEAR ENGINEERING DEPARTMENT BROOKHAVEN NATIONAL LABORATORY

ORGANIZATION CHART

1968

Reactor Physics Division

J. CHERNICK, H. KOUTS

Reactor Physics Theoretical Group

PULSED NEUTRON EXPERIMENTS IN FAST REACTORS

An analysis of pulsed neutron phenomena in the fast domain has been performed. The dispersion relation yielding the time decay for a fast multiplying system has been established by using a scheme valid for both diffusion and asymptotic transport theories. The scheme requires explicit knowledge of the Green's function for the time-dependent slowing-down problem; closed form expressions for the Green's function and the related reaction rates were obtained under the assumptions of simple cross-section models (constant plus $1/v$) and a synthetic Greuling-Goertzel kernel representing elastic slowing down. (With the use of Waller's results for exact elastic scattering, it was possible to establish the corresponding more general but cumbersome dispersion law.)

The dispersion relation of a fast multiplying system, obtained under the preceding assumptions, has been extensively studied. It has been shown that, in general, no complex decay modes and at most one real isolated mode may exist. Further, it has been shown that beyond some maximum system buckling no discrete decay mode exists. This result is analogous to thermal pulsed systems.

In order to rigorously investigate the "disappearance of the discrete mode into the continuum," the dispersion law has been analytically continued. Beyond the maximum buckling, roots of the analytic continuation were found on the adjacent Riemann sheets. An asymptotic expansion was made in the neighborhood of the branch-point and the maximum buckling. The nature of the N -furcation and the motion of the roots on the adjacent Riemann sheets were found to depend sharply upon the fast system enrichment.

A thorough asymptotic evaluation was performed for the integrals representing reaction rates. It was confirmed that the roots on the adjacent

Riemann sheets, when located sufficiently close to the real axis, corresponded to near exponential decay for a limited time interval ("pseudo-modes"). These theoretical investigations explain experimental results recently obtained in European experiments on the fast pulsed assemblies "SUAK: AND EURECA," which covered a wide range of subcriticality. J. DORNING, B. NICOLAENKO, J. THURBER*

REACTOR KINETICS

Nonlinear Space-Independent Kinetics

A general perturbation method, based on the dominant linear roots, has been developed to predict the permissible bounds on initial disturbances in linearly stable systems. It is analytically straightforward and gives realistically large bounds, for both linear and nonlinear feedback, in parameter regions that were previously considered unsafe (i.e., regions with finite escape time). Although a Lie series method can give larger bounds (bounds which may be unnecessarily large), the present method is quicker and gives one or two-dimensional results, for n -dimensional equation systems, which can be interpreted in a much more straightforward way than those obtained with Lie series.

Application was made to three specific reactor models, including xenon feedback and an excursion model. The main practical application of the method is in analyzing existing safety models of reactors to allow the relaxing of overly stringent safety requirements for a wide class of future reactors and, in particular, fast reactors with positive void coefficients.

L. SHOTKIN

Nonlinear Space-Time Kinetics

A comparison was made between modal expansions and iterative methods in both nonlinear space and space-time problems. The modal expansion was found to be best for space problems

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and the iterative technique best for space-time problems. If L is a linear self-adjoint operator and $N(\phi)$ is a nonlinear functional of ϕ , then the iterative technique may be written

$$L\phi_0 = 0, \quad (1a)$$

$$L\phi_n = N(\phi_{n-1}), n = 1, 2, \dots \quad (1b)$$

In order for Eq. (1b) to possess solutions, it is required that $N(\phi_{n-1})$ be orthogonal to ϕ_0 , i.e.,

$$\int_{\text{reactor}} \phi_0(x) N[\phi_{n-1}(x)] dx = 0. \quad (2)$$

Equations (1) and (2) were applied to the Fuchs-Nordheim model for fast reactor transients, and were found to give reasonable answers with a minimum of effort. Further, the solutions were valid for much larger initial disturbances than were solutions obtained by an approximate modal analysis. L. SHOTKIN

Effect of Delayed Neutrons on Power Oscillations

When considering periodic solutions of the nonlinear point kinetics equations, it appears that the delayed neutrons have a considerable effect on the general analytic results. For a given range of reactor parameters, the delayed neutrons appear to determine the character of the periodic oscillations. The inclusion of the delayed neutrons thus allows previously developed methods to be used to investigate a wider variety of reactor stability and boundedness problems. D. HETRICK, L. SHOTKIN

Corrections to the Prompt-Jump Approximation

In this work a formal representation for the reactor power is developed in terms of a small parameter (the prompt neutron lifetime divided by the delayed neutron fraction). From this result one is able to put the prompt-jump approximation on a firm theoretical basis and to improve upon previous results. Compact analytical results have been obtained for the case of one group of delayed neutrons. For the six-delayed-neutron case, accurate numerical solutions may be obtained with constant, reasonably large time steps. These solutions are more accurate than those obtained from lower order techniques requiring variable time steps. R. GOLDSTEIN, L. SHOTKIN

FLUID DYNAMICS

Two-Phase Flow

Analysis of a condensing flow experiment of Goodykoontz and Dorsch has confirmed the existence of a crucial condensing length, in analogy to the crucial boiling length in boiling flow. With this concept it was possible to correlate the stability data in terms of the parameters that are important in defining the steady-state condensing length. These can conveniently be combined into a single dimensionless parameter, E , with

$$E = \frac{Q_{\text{sat}}}{GH_{gl}x(L)},$$

where Q_{sat} is the heat removed from the two-phase fluid with mass flow rate G , H_{gl} is the latent heat of vaporization, and $x(L)$ is the quality at the channel inlet. At steady state $E = 1$, and the departure of E from unity is a measure of channel instability. It appears that, for a given condensing length, increasing E increases stability. L. SHOTKIN

Numerical Solution of the Navier-Stokes Equation

The developmental work on the numerical solution of the Navier-Stokes equation has been essentially completed. At the present time a study is being conducted to determine whether or not the numerical methods developed at Brookhaven and at other places can be fruitfully applied to problems related to the safety of sodium-cooled reactors. In particular, problems relating to bubble migration at the inception of boiling are being considered. P. MICHAEL

RESONANCE ABSORPTION

Iterative Solutions by Means of Trial Operators

The trial operator approach of making mathematical approximations has yielded significant results for reactor problems. In this approach, an iterative solution to the mathematical equations of interest are obtained in terms of a trial operator. The operator is then fixed by requiring that successive terms in the iterative series vanish. The analytical results obtained in this way are in some ways similar to those obtained by variational calculations. However, the iterative method yields much additional information, such as error estimates and the sign of the error. Thus, for example,

this approach provided quite narrow bounds to a resonance integral calculation. For such non-self-adjoint problems, these bounds are particularly difficult to obtain by other means.

As a specific numerical example, for the 192-eV intermediate resonance of U^{238} in a 1:1 atomic ratio mixture with hydrogen, the iterative results were $0.159\text{ b} < I < 0.165\text{ b}$ for the resonance integral bounds. A numerical evaluation of the integral equations gives 0.161 b for the "exact" resonance integral. The exact result is seen to fall nicely between the predicted bounds. The corresponding variational calculation for this problem yields 0.173 b for the resonance integral, so that the iterative results are approximately a 5% improvement over the variational estimate. R. GOLDSTEIN

NEUTRON THERMALIZATION

Small System Extrapolation Distances, and Neutron Diffusion Parameters

Size-dependent extrapolation distances for small spherical light-water systems have been calculated using the pulsed neutron experiment asymptotic decay constant as a consistency criterion between exact transport theory and asymptotic reactor theory. These size-dependent extrapolation distances corrected erroneous values that had existed in the literature. The neutron diffusion coefficient and the diffusion cooling coefficient for H_2O were also determined from the asymptotic reactor theory calculations (performed for both the pulsed and the static or poisoning experiments). The agreement of these parameters with the accepted experimental values was excellent. J. DORNING

Neutron Pulse, Wave, and Poisoning Experiments

Three separate investigations into the pulse, wave, and poisoning experiments were carried out. The investigations centered on the theoretical interpretation and explanation of these experiments when the independent experimental parameter is permitted to exceed the crucial value that causes the variable to be determined to transcend a natural physical barrier (the minimum reaction rate for the pulse experiment and the minimum cross section for the wave and poisoning experiments). The analyses, performed via model transport equations, were carried out in such a way that the solutions represented detector responses rather than neutron

Figure 1. Trajectory of the dominant root of the pulse neutron experiment dispersion law.

fluxes or number densities; thus, their relationship to the quantities observed experimentally was immediate.

In the analysis of the pulse neutron experiment it was found that when the buckling exceeds the crucial value B^* the dominant root of the analytically continued dispersion law in the time-transform plane bifurcates forming complex conjugate roots on the nonphysical sheets of the Riemann surface (see Figure 1). The asymptotic time-dependence, given then by a branch integral, is dominated by these roots which cause the integrand to take on a Lorentzian shape along the branch cut.

Similarly, analysis of the poisoning or static experiment shows that bifurcation of the dominant root in the space-transform plane occurs as the absorber concentration exceeds the crucial value ρ^* . In this case the bifurcated roots also move off the physical sheet onto adjacent Riemann sheets; however, here the rate at which the roots depart from the associated axis and branch-cut is much slower than that which describes the pulse problem roots. Thus, near-exponential behavior is even more strongly indicated in this case.

Investigation of the neutron wave problem has shown that when one considers the detector response, a purely discrete root of the analytically dispersion law exists even when the source frequency exceeds the crucial frequency ω^* . However there is competition with a branch contribution, but the pole will dominate yielding purely discrete behavior in most of the so-called continuum region.

In all three cases the results stated above have served as an explanation of the apparent paradoxes between the experimentally observed discrete behavior and previous theoretical predictions which had ruled out discrete phenomena.

J. DORNING, J. THURBER*

Reactor Physics Analysis Group

Space-Energy Synthesis

In many critical experiments much of the reactor volume will not be far distant from region boundaries. A synthesis approach, which develops the reactor flux in terms of basis spectra appropriate in some sense to each of the various regions involved, appears to be a productive approach to the analysis of critical experiments.

A study based on variational techniques has been made of the overlapping group method in the space-energy synthesis of fast reactors. An idealized, two-region (core and reflector) reactor analyzed by a multigroup S_n code served as a standard against which to test the efficiency of the overlapping group method. In contrast to previous work, a full transport theory treatment is adopted instead of diffusion theory.

The traditional approach, assuming energy spectra characteristic of the infinite medium spectra of the reactor subregions, was inadequate to predict reaction rates throughout the whole reactor although the reactivity is accurately determined.

Refinements, all of which showed improvements to calculated reaction rates, included (1) adopting alternative trial energy spectra, (2) determining both space/angle and energy variations of the trial functions by the variational principle, (3) permitting different predetermined energy spectra in different parts of the reactor – discontinuous trial functions, (4) combining (2) and (3) for even greater flexibility, and (5) using a variational principle giving second-order estimates of parameters (e.g., reaction rates) other than the eigenvalue, and proceeding as in (2).

The method is evidently capable of providing accurate estimates of the reactivity, reaction rates, and spatial fluxes, although probably not all in the same calculation. However, there are difficulties in the straightforward application of the method, not least of which is choosing a variational functional

which we can guarantee will give a stationary point for a particular trial function. M. LANCEFIELD

Analysis of Pu-Al-D₂O Lattice Experiments

A critical analysis of poisoned Pu-Al-D₂O lattice experiments at BNL is under way. Because of the thermal poisoning present, this will provide a test of the epithermal cross sections of Pu²³⁹ as well as of the other constituents of the lattices. The basis of the analysis is the use of the evaluated nuclear data file (ENDF/B) cross section data, modified as necessary, together with the best available calculational methods.

Preliminary work with moments and Monte Carlo calculations has shown that the deuterium cross section is too small to give agreement with the measured age in D₂O. Alteration of the cross section to give agreement with the age also brings it into better agreement with values commonly used before the ENDF/B compilation.

The HAMMER code has been used for a number of fundamental mode calculations for the experimental lattices. At the same time Monte Carlo calculations with the use of the MOCA code have been made for the same lattices. The reaction rates in the high energy region (above about 275 eV) are different in the two sets of calculations, and the more rigorous values obtained from Monte Carlo work are being used to correct the values from HAMMER.

Additional programming has been necessary for a number of purposes. A cross-section preparation code has been written to provide MOCA library cross sections from ENDF/B data. Alterations and corrections have been made in some of the data preparation codes for use with HAMMER.

Because of the presence of Pu²⁴⁰ in these lattices, it is necessary to extend the thermal cut-off to higher energies than those previously used. This is in order to include the lowest Pu²⁴⁰ resonance within the range of the THERMOS portion of HAMMER. Consideration has been given to increasing the number of THERMOS groups to accomplish this. However, this has not been found to be necessary. Instead, fewer groups are used at very low energies so that higher energy groups can be incorporated. Calculations of thermal spectra in typical poisoned lattices have shown that this procedure should be correct, since the poisoning strongly depletes the neutron flux at the very low energies where the groups have been coarsened.

*Member of the Applied Mathematics Department.

As results are obtained from the present lattice calculations, various choices other than that of ENDF/B will be made for the Pu^{239} cross section in the high energy region. Comparison of calculation and experiment should show which set of cross-section values and in particular which capture-to-fission ratio, α , is best.

O. OZER, T. SHIMOOKE,
M. LEVINE

Testing ENDF/B Data Against Integral Experiments

Comparison of ENDF/B data against integral experiments requires the use of Monte Carlo methods in addition to fundamental mode and transport methods. The REPTITIOUS Monte Carlo code has been of great importance in analysis of lattices with resonance capture. This code is being modified in order to be able to exploit the detail on resonance parameters and cross sections in ENDF/B. This alteration is also translating the code into the Fortran language from the original FAP. Thus the results will be more representative of the ENDF/B data and at the same time the code will be faster and easier to run on the CDC 6600 computer. The new version of the code will also be a valuable tool for the analysis of fast reactor criticality and Doppler effects.

W. ROTHENSTEIN

Codes for Fast Reactors

Computer routines for processing ENDF/B data have been worked on intensively. Debugging and conversion for use on the BNL computer have been carried out on a number of codes including MC², ETOE, DAMMET, and others.

Codes for fast reactor calculations including two-dimensional diffusion theory and burnup (2DB) and the S_n method (DOT) have been obtained and converted for use on the BNL computer.

Many of the codes that were in working order on the computer have become inoperative because of the change in computer operating system from Scope 2 to Scope 3 which the Applied Mathematics Department has introduced. Large efforts have been required and will continue to be required to restore these codes to use under the new system.

A. ARONSON

Fast Reactor Calculations

Calculations were done for participation in the CSEWG intercomparison on ZPR3 Assemblies 11 and 48. Reactivity effects, activation rates, and perturbation effects have been studied using ENDF/B data with associated service routines and reactor codes.

A. ARONSON

Analysis of Fast Reactor Critical Experiments

With the use of ENDF/B data, criticality computations have been made for some of the Livermore plutonium assemblies. The MC² code in the fine group mode was used to produce group cross sections for the S_n transport analysis. Additional work in analyzing these experiments is being planned in order to use the ultrafine mode of MC² and to test the effect of alterations in the Pu^{239} cross sections.

A. ARONSON, J. CHERNICK

Fast Neutron Transport

The transmission of fission spectrum neutrons through a large sodium block has been studied by means of the S_n transport method. This is for the purpose of deducing information concerning fast spectrum cross sections from transmission experiments. The emergent spectrum has been studied, for various block sizes, to determine its sensitivity to choice of energy group structure. By using finer and finer resolution within a resonance it was possible to determine just what resolution is required for adequate representation of the effect of the resonance on the spectrum. A code for preparing ENDF/B data for use in the experimental S_n calculations was obtained and converted for use on the BNL computer.

J. WAGSCHAL, M. LEVINE

Calculations for Measurement of Pu^{239} Capture-to-Fission Ratio in the HFBR

Calculations have been made to help plan the measurement of the Pu^{239} high energy α in the HFBR. Irradiation of a Pu^{239} foil wrapped in boron will allow the capture-to-fission ratio to be measured for the epithermal energy range. The spectrum inside the boron wrapping has been computed approximately for various boron thicknesses, and reaction rates have been computed for various possible Pu^{239} cross-section variations.

More precise calculations will be made, by using higher transport theory methods, to analyze the actual experimental results.

T. SHIMOOKE

Xenon Modal Stability

A detailed study of first harmonic stability in one and two-dimensional models of bare and reflected cores was completed, and a paper covering the pertinent results has been prepared for publication.

G. LELLOUCHE

Space Time Analysis

Three portions of the NOMURK Reactor Dynamics System have been completed this year: (a) NØDE,

Figure 2. Axial sensitivity function.

a multitemperature (up to 50) space-independent code accounting for xenon effects; (b) NØABE, a two-dimensional static power shape code accounting for space-dependent fuel cladding and coolant temperatures and allowing space-dependent reactivity coefficients; and (c) NØAH, a code that solves the one-energy group one-dimensional space-time diffusion equation accounting for three temperatures, xenon, and six delayed neutron groups. This code is a combination of two earlier (internal use) codes, NØAH and XENØN. A user's manual has been completed and publication of the code is imminent. Studies of algorithms for use in multigroup and two-dimensional versions of NØAH are under way.

An analysis of various Spert excursions has started. Early results show that extensive power shape distortion occurs immediately after the peak power has been reached. In order to more accurately represent the post peak behavior, programming of the two-phase hydrodynamic equations for use with NØAH is under way; this will permit the study of boiling phenomena.

G. LELLOUCHE

Reactor Safety Analysis Evaluation

External Detection of Reactor Power Shapes

To insure that local power generation rates in a Pressurized Water Reactor (PWR) do not exceed allowable values, it is common to provide a number of flux detectors inside the core. Instruments outside the core do not provide as much detail about the power shape, but in some cases they may supply enough information to show when the in-core instruments should be inserted in order to

Figure 3. Radial sensitivity function $G_r(r)$ vs r .

examine questionable situations. A study was made of the response of external detectors to power shape changes in a PWR. This was done by introducing the Green's function for each instrument. Each instrument in this case was a line detector located outside the pressure vessel and of length half the core height. It was assumed that there were four pairs of such detectors located at 90° intervals around the circumference above and below the midplane of the reactor. Here the Green's function describes the response of any detector to a unit of power generated at some point in the core and is a function of the position of this point. Once this sensitivity function is obtained, it can be folded with any desired power distribution to obtain the response of the instrument to that power shape.

It was shown that one and two-dimensional diffusion theory is sufficiently accurate for this problem and that the sensitivity function is separable with satisfactory accuracy in the usual cylindrical coordinates. The axial and radial sensitivity functions are shown in Figures 2 and 3.

The sensitivity function found here was used with a number of tilted power distributions to show the correlation between instrument response and the peak-to-average power ratio associated with power tilting.

M. LEVINE

Oyster Creek Review

A review of the xenon stability of the Oyster Creek Direct Cycle Boiling Power Reactor was carried out for the Division of Reactor Licensing

(DRL). It was determined that while none of the usual temperature feedback models can be used to correctly mock up void formation, the Oyster Creek Reactor was probably stable against spatial oscillations at least at beginning of life.

G. LELLOUCHE

Moderator Temperature Coefficient

Since the moderator temperature coefficient of a pressurized water reactor cannot be measured under operating conditions but must be calculated, it is important to check the calculation method against whatever experimental information is appropriate. Information obtained through DRL on measurements of reactivity vs water temperature and dissolved boron concentration in zero power experiments were used for testing. The HAMMER lattice code was used to obtain group constants for each temperature and boron concentration which were then used in diffusion theory calculations of reactivity. The results show generally good agreement between calculated and measured reactivities.

The model used in the calculations ignored control rods that were present in the experiment. Calculations are proceeding to find the effect of these on the coefficients.

L. EPEL

Fuel Rod Bowing

The reactivity effect of fuel rod bowing was studied for simple fuel rod displacements. The relationship between reactivity change and the magnitude of the displacement causing the change was studied over a wide range of displacement both inward and outward.

Mechanisms that might cause such displacements have not been studied as yet. However, the results obtained here are expected to be useful in the study of explicit fuel motion effects.

L. EPEL

Effect of Local Perturbations on Global Power Shape

The effect on reactor power shape of moving of an interior control rod was studied in order to help assess the role of external power detectors. Figure 4 shows the power shapes at the core surface and in the interior for a central control element fully and partially withdrawn. The axial power distribution near the outside is practically unchanged although the interior power distribution is severely altered by the presence of the control rod.

Since it is mainly the peripheral power generation that affects the external instruments, this

Figure 4. Influence of control rod on power shape.

shows how difficult it is to detect such rod motion from outside the core. It is expected that similar considerations will apply to other localized perturbations.

J. HOOPER

Control Rod Worth

Calculational methods are being developed to study control rod worth. Comparisons are being made with available experimental information to test these methods.

D. DIAMOND

Reactor Physics Experimental Group

SMALL REFLECTED ASSEMBLIES

A technique to analyze small reflected assemblies and some of the problems encountered in this analysis was outlined in the last annual report; since then, this work has been completed. Briefly, the method of analysis is based on the DSN code ANISN and it corrects the tendency of diffusion theory to underestimate the reactivity.

To appreciate the method more fully, a series of BNL exponential experiments was studied. The cores were fueled with UO_2 , moderated by water, and surrounded by an effectively infinite water reflector. With the use of the measured axial buckling, four-group calculations were carried out by conventional means, i.e., diffusion theory, and by the DSN method. The necessary four-group constants were obtained from the four-group edit of the HAMMER code. Table 1 lists the radii, measured

Table 1

Core No.	Core parameters		Value of k_{eff}	
	Core radius, cm	Axial buckling, cm^{-2}	λ_{s_8}	λ_{DT}
1	11.5211	-0.009992	0.993008	0.970621
2	13.4757	-0.007333	0.994266	0.977287
3	15.6561	-0.004985	0.992187	0.978792
4	18.2499	-0.003003	0.993604	0.982825
5	22.9890	-0.000630	0.997038	0.988955

Table 2

Core 1

$\Delta = (\tau B_m^2)S_8 - (\tau B_m^2)DT,$			
$\tau = \frac{D}{\Sigma_a + \Sigma_r}, \quad \Sigma_r = \text{removal cross section}$			
Group	$(\tau B_m^2)S_8$	$(\tau B_m^2)DT$	Δ
1	0.366252	0.445762	-0.079510
2	0.224813	0.235725	-0.010912
3	0.046768	0.035824	0.010944
4	-0.275698	-0.288651	0.012953

axial bucklings, and values of k_{eff} . These values of k_{eff} indicate that the diffusion theory determination decreases in value with decreasing core size. This is because the small cores are more dependent on an accurate determination of leakage. This inadequacy in diffusion theory may be better understood by comparing values of τB_m^2 determined by the two methods of calculations. Table 2 gives the respective values of τB_m^2 and their differences for each group for core 1. From the table it can be seen that for the first two groups $(\tau B_m^2)DT > (\tau B_m^2)S_8$. This indicates that diffusion theory underestimates the worth of the reflector in these two groups. In groups 3 and 4 the opposite trend takes place, but only slightly. The increased leakage in diffusion theory explains the low values of k_{eff} .

The discrepancy illustrated in Table 2 may be used as a criterion for systematically adjusting the values of the diffusion constant, D , in the reflector. These values are so chosen to eliminate the discrepancy in the case of all the cores studied. The results of this procedure are illustrated in Figure 5 where the modified values of D in the reflector are plotted against $1/R_c$ (R_c =core radius) for each group. The three epithermal constants suggested

Figure 5. Variation of corrected diffusion coefficients in the reflector with core radius.

by Eich and Williams [*Nucl. Sci. Eng.* **24**, 209-11 (1966)] are seen to be in acceptable agreement.

A calculational effort in support of the Pu-Al fueled heavy water moderated exponential experiments is being carried out. At the present time the necessary codes and cross-section sets are being prepared for this analysis. The salient point of interest in this analysis is the value of α for Pu²³⁹ in the keV range. In addition, calculations are being carried out with the use of the one and two-dimensional DSN codes ANISN and DQT, respectively, in support of the fast reactor heterogeneity experiments.

H. LUDEWIG

ANALYSIS OF BNL U²³⁵-GRAPHITE CRITICAL EXPERIMENTS

With cross-section data derived largely from the ENDF/B, an analysis of the nearly homogeneous enriched uranium graphite critical assemblies was carried out. These assemblies are characterized mainly by their high leakage rate, and two methods were used for estimating the leakage: (1) the conventional B_1 approximation, and (2) the moments method using Monte Carlo calculations.

It was found that the B_1 method describes the leakage quite accurately. Briefly, the calculated results for k_{eff} , neutron lifetime, and foil activation ratios are in excellent agreement with measurements. This work is now complete. B. SEHGAL

SOLID-STATE FISSION TRACK DETECTORS

It has been determined that the solid-state fission track detector technique of measuring fission rates is a useful tool in experimental reactor physics. Measurements have been made of absolute fission rates of U^{233} thin film sources in thermal neutron fluxes calibrated by absolute gold foil measurements. Results have shown that the technique is $>95\%$ efficient. The technique has been used to measure fast fission ratios in $\text{U}^{233}\text{O}_2\text{-ThO}_2\text{-D}_2\text{O}$ lattices and for absolute power calibrations of two low power critical assemblies, FS-1 and CEPFR.

Visual counting of the fission tracks is tedious and time-consuming work, and an effort has been made to automate it. The technique chosen involves photographing the tracks and scanning the film on a flying spot digitizer designed for scanning spark chamber film. Careful control is required in the three steps of etching, photographing, and scanning to obtain reproducible results.

The etching has been standardized with a well regulated temperature bath, carefully controlled NaOH concentrations, wetting agent (DOW FAX 2A1), and a rotating wheel for holding the foils. It was discovered that the track quality is a function of the length of time between exposure and etching. If the foil is etched immediately after exposure, the tracks are of very poor quality. A waiting period of two days was found to be necessary to obtain optimum track size.

The foils are photographed at $40\times$ magnification using 35-mm Kodalith high contrast film. The use of this film requires that the light source be extremely stable. This is achieved through a well regulated dc power supply and constant monitoring of the light intensity. Accurate development is obtained by making use of the automatic Kodalith processor maintained by the Photography Group.

The flying spot digitizer generates an intense $20\text{-}\mu$ spot of light that sweeps across the moving film. A photomultiplier located behind the film detects a flash of light each time the spot crosses a track on the film. An amplifier, discriminator, scaler system

is used to relatively count the number of tracks present. W. TUNNEY, E. WEINSTOCK

COMPILATION OF FAST REACTOR EXPERIMENTS

The testing of analytical methods and cross-section sets in fast reactor physics requires a critical selection of pertinent experimental information. The growing number and diffuseness of sources of such information makes this selection increasingly difficult; furthermore, it becomes increasingly important to avoid redundancy in this activity.

In light of these considerations, work has begun on a compilation of fast reactor experiments, which will include all significant experimental information of sufficient "cleanness" and accuracy to be useful in testing analytical methods and cross sections. This experimental condition, as well as the results, will be described in sufficient detail so that direct use can be made of the information reported. As well as being a vehicle for assembling recent fast reactor data, the compilation will also provide the opportunity of presenting a re-evaluation of older data, with the most recent estimates of experimental corrections, etc.

A preliminary format for the compilation, including a number of sample entries, has been reviewed by the European-American Committee on Reactor Physics, the Atomic Energy Commission, and the various laboratories in the world engaged in fast reactor experimentation. The work of evaluation and compilation is now under way.

P. PALMEDO, R. HOEFLING, J. CONANT

MEASUREMENT OF DELAYED NEUTRON PARAMETERS

An analysis performed during the year demonstrated that a need exists for a new series of measurements of delayed neutron parameters. Of particular importance is a more detailed measurement of the spectra of the various delayed neutron groups. The analysis also showed that a new experimental approach to the measurement of delayed neutron parameters, originally proposed by G.S. Brunson and R. J. Huber, afforded distinct advantages over previous methods, particularly in the determination of spectra.

The experiment consists basically of passing a continuous band containing the fissionable material past a neutron source and counting delayed

neutrons at some distance from that source. By varying the speed of the tape the various delayed neutron groups can be emphasized, and individual yields and half-lives can be readily derived from the composite data. Of particular importance is the fact that at each tape speed one can measure a spectrum that is constant in time.

In a closely related but distinct part of this project, a measurement will be made of the total delayed neutron fraction, β . The basic approach will be simply to compare the neutron production rate of a sample in a neutron beam with the production rate after the beam is interrupted. The basic simplicity of this relative measurement promises a successful competition with the standard approach in which two kinds of absolute measurements are required.

Preliminary work on this experiment has proceeded in two areas – the development of tapes used to transport the fissionable material and the development of detector systems. Sample tapes are currently undergoing tests on a device designed specifically to test tape endurance and fuel loading techniques. A detector system with an almost flat energy response has been constructed according to a design developed at Los Alamos. This system is being used in preliminary tests of the method of measuring β . The measurements of delayed neutron spectra will rely heavily on the proton recoil proportional counters whose development is described in another section of this report.

J. CONANT, P. PALMEDO

FAST NEUTRON SPECTROSCOPY

Work has continued on the development of a fast neutron spectrometer employing proton recoil counters suitable for use in fast reactor cores. Having developed techniques for constructing and filling methane and hydrogen proportional counters to obtain energy resolutions of the order of 4% (for the 615-keV $N^{14}(n,p)C^{14}$ line), emphasis shifted to the development of the electronics and computer routines for γ -subtraction by pulse shape discrimination. More recently, the compatibility of the electronic and analytical components of the spectrometer system has been studied by taking preliminary spectra of a Pu^{239} -Be source and of a beam from the FS-1 fast critical assembly.

A study of the energy dependence of rise-time spectra employed in the pulse shape discrimination

showed an apparent decrease in rise-time with increasing pulse height. This is due to the sampling method used to measure rise-time. Although the pulse height dependence could be reduced by electronically dividing the rise-time signal by the energy signal as in Bennett's spectrometer at ANL, it was decided to develop a computer routine for γ -subtraction that would locate the proton recoil peak in the rise-time spectrum. This option was chosen to avoid additional complication of the electronics that might impair resolution. Problems in overlapping segments of the recoil pulse distribution into a continuous spectrum over the full energy range were traced to the pulse-height dependence of the rise-time spectra. These problems were eliminated by appropriate electronic settings in the fast channel.

In order to develop a suitable computer code to extrapolate the proton recoil rise-time peak in the region of overlap with the γ distribution, the shape of the recoil peak was studied in rise-time spectra obtained from a Pu^{239} -Be source, a Pu^{238} -Li source, and a beam from the FS-1 assembly. An apparent γ peak at energies well above the maximum likely γ -energy deposit was traced to high energy, low dE/dx recoil protons. A γ -subtraction code has been written to integrate under the extrapolated proton recoil peak, while providing flexibility for handling the long proton tracks where they are significant. In addition, rise-time spectra of the first FS-1 run suggest that the γ background in the external beam may not be a serious problem.

The compatibility of the separate stages of electronic pulse analysis, γ -subtraction, and final unfolding of the neutron spectrum was checked by obtaining preliminary spectra of a Pu^{239} -Be source and of a beam from the FS-1 assembly. Both spectra were obtained with a methane recoil counter. Unfolding of the neutron spectra, uncorrected for end and wall effects, was carried out by the QUICKDIRT code written by P. Palmedo. The early Pu-Be spectra show two peaks in the 0.2 to 1.6-MeV energy range. Such peaks are not inconsistent with the Pu^{239} -Be spectrum calculated by Anderson and Bond, although reported experimental spectra do not indicate the second peak. The preliminary FS-1 beam spectrum (Figure 6) locates a peak in the 650-keV region predicted by the 99-group GAM II calculation for the core center. Other features of the measured and calculated spectra show some encouraging similarities. The large peak in the low energy region of the mea-

Figure 6. Preliminary FS-1 beam spectrum.

sured spectrum is unaccounted for, and contributions from room return and collimation through the steel reflector are being studied as possible sources of these low energy neutrons. The Pu-Be and FS-1 spectra were obtained primarily to test the compatibility of the electronic and analytical stages in generating neutron spectra, and their spectral information is considered highly tentative. Work is under way to confirm the reproducibility of these early results and to test the performance of the spectrometer against a known spectrum produced at the BNL Van de Graaff.

H. KOENIGSBERG, C. SASTRE

FAST SOURCE REACTOR

The fast critical assembly machine (FS-1) has been brought critical and a number of measurements of its operating characteristics have been performed. Some preliminary experiments have also been performed.

The core of FS-1 consists of highly enriched (93.2% U^{235}) uranium metal, in the form of thin foils clad in type 347 SS, and graphite moderator plates. A typical cell in one half of the core (the assembly is of the split-bed type, with one half the core fixed and the other movable) consists of a standard fuel "pack" containing 2.665 kg U, 1.658 kg SS, and 1.494 kg graphite. The nominal cell thicknesses of these materials are 0.043, 0.060, and 0.500 in., respectively. The actual (rather than nominal) volume ratios are $V_G/V_U = 11.61$ and $V_{SS}/V_U = 1.345$; the corresponding atom ratios are N_G/N_U

$= 19.61$ and $N_{SS}/N_U = 2.389$. The core is reflected on all sides by ≈ 20 in. of steel.

The critical mass of the first core constructed was 168.8 kg U. This core contained five control rods, each loaded with a standard fuel pack.

For the second core, one of the control rods was removed in order to permit the insertion of a test box containing carefully machined test plates of enriched uranium, stainless steel, and graphite in approximately the same proportions as those of the core. The purpose of the test box is to provide a well-defined geometry for heterogeneity and reaction-rate measurements. In order to accommodate the test box, whose dimensions are $3.25 \times 3.25 \times 10$ in., it was necessary to cut some of the standard fuel elements and graphite plates in the fixed half of the core. A loading of 152.2 kg U resulted in a reactivity of $\approx 25\epsilon$ for this core.

Subsequently it was found that varying the size of the opening in one of the beam holes in the reflector is a convenient way of shimming the reactivity of the assembly without altering the core. This is done simply by inserting or removing steel reflector bars in the beam hole. With the hole approximately half full the critical loading was 1.55.2 kg U, 173.8 kg graphite, and 97.6 kg SS.

Various operating characteristics have been determined for the assembly. Rod worths, both total and differential, have been measured, as has been the reactivity as a function of distance between the fixed and movable halves of the core. A measurement with a tank of water next to the reflector showed that neutron reflection from outside the reflector has a negligible effect on the criticality of the assembly.

Of some concern was the effect that compressing the core might have on criticality. In one experiment, therefore, the volume of $\approx 30\%$ of the core was reduced by 1% (by driving small shims in above the core to compress it). The resultant increase in reactivity was 14ϵ , too small to constitute a hazard but large enough to affect the reproducibility of certain types of measurements.

Preliminary experiments on neutron streaming in the reflector have been performed. The reactivity of the assembly was measured with two different inserts in a central beam hole. Both inserts were composed of $\frac{1}{4}$ -in.-thick steel plates separated by $\frac{1}{4}$ -in.-thick air gaps, but in one case the plane of the plates was perpendicular to the axis of the beam hole and in the second case it was parallel to it. No difference in reactivity was ob-

served in the two cases. The flux distribution along the axis of the beam hole was also measured by exposing U^{235} foils in each of the inserts and counting the resultant fission product activity. No difference was found in the two distributions. It is concluded that streaming effects cannot be conveniently measured in test regions of the size used for these experiments (the cross sectional dimensions of the beam hole were $\approx 4\frac{1}{2} \times 4\frac{1}{2}$ in., compared with roughly 24×24 in. for the cross section of the core).

Measurements of the neutron spectrum at the edge of the core have also begun and are described in another section. P. PALMEDO, E. WEINSTOCK, K. DOWNES, A. COURT

Pu-Al-D₂O LATTICES

A series of exponential experiments utilizing plutonium-aluminum fuel rods in heavy water are in progress to provide integral data that may be used to test plutonium cross sections. The lattices are undermoderated in order to emphasize the importance of neutron cross sections in the epithermal energy range. In particular, uncertainties in the capture-to-fission ratio (α) for plutonium make these experiments of interest to LMFBR and plutonium recycle projects.

A preliminary series of six lattices were conducted with varying moderator-to-fuel volume ratios and various amounts of boron dissolved in the heavy water. These series were used to develop the experimental techniques which are now being used for a complete series of ten or more lattices. The data from the preliminary series were also used to deduce a preliminary value of α for plutonium. Measurements of buckling with indium foil activations indicated that there was not a unique material buckling in at least three of the lattices, i.e., the material buckling was spatially dependent. It was concluded that neutrons reflected from a paraffin shield nearby were perturbing the neutron spectrum throughout the lattice. The paraffin shield was subsequently replaced by a borax shield and the subsequently measured flux distributions indicate a constant material buckling over most of the lattice volume.

Activation and cadmium ratio measurements have been completed in the Pu-Al-D₂O lattice with a moderator-to-fuel volume ratio of 1:1. These measurements provide an integral check on the spectral calculations.

Table 3

Activation and Cadmium Ratios, Clean 1:1 Pu-Al-D₂O Lattice. (Data not corrected for self-shielding.)

Detector	A* (relative to Mn)	Cadmium ratio
Au	9.02 $\pm$ 0.07	1.024 $\pm$ 0.005
In	7.21 $\pm$ 0.05	1.105 $\pm$ 0.008
Mn	1.00	1.090 $\pm$ 0.010
Pu ^a	0.358 $\pm$ 0.003	1.80 $\pm$ 0.02

^aFission.

The method is identical to the one used in the experiments on the enriched uranium-graphite assemblies previously reported. Dilute foils of selected materials are exposed in the lattice, the resultant activity is measured, and the foils are then exposed in a known reference spectrum (in this case that of a graphite thermal column) and the activities are measured again. The activation ratio of a pair of detectors x and y is defined as

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

where A is the activity and the subscript r stands for the reference spectrum.

The detectors were dilute foils of Au, In, Mn, and Pu. These were exposed near the cell boundary in the moderator. The Pu foils were gamma-counted and the remaining foils both beta- and gamma-counted. Measurements could be carried out in the clean lattice only, the fluxes in the poisoned lattices being too low. The results are shown in Table 3, together with the cadmium ratios (cadmium thickness ≈ 0.045 in.). The latter are not as useful as the activation ratios, since (1) the values for all detectors except Pu are so close to unity, and (2) the close proximity of the cadmium covers to the fuel rods undoubtedly results in a severe perturbation in the flux, particularly for the Pu detectors. The small value of Cd.R. - 1 does show, however, that the spectrum in the lattice is strongly epithermal.

The data in Table 3 have not been corrected for self-shielding, which, however, is expected to be small (about 4% in the activation ratio of Au and <1% for the remaining detectors). Calculations of the activation and cadmium ratios are being performed in order to compare the experimental results with theory.

G. PRICE, R. SCHILLER,
K. CHANDRAMOLESHWAR, E. WEINSTOCK

CALIFORNIUM EXPERIMENT

Measurements have been completed and analyzed of the production of Cf^{254} by the successive capture of two neutrons in Cf^{252} .

In this experiment, a 0.01- μg sample of Cf^{252} enclosed in a cadmium cover was exposed for 20 days to the flux in the V-15 facility in the core of the Brookhaven High Flux Beam Reactor (HFBR). The epithermal flux per unit lethargy at this location is 8×10^{13} n/cm²-sec (obtained from the exposure and counting of dilute gold and cobalt foils in this facility). Following the exposure, the sample and an unirradiated 0.1- μg sample of Cf^{252} , used as a standard, were counted periodically for ≈ 3 months. The detection system consisted of six BF_3 counters imbedded in paraffin. The counters detected the neutrons emitted in the spontaneous fission of Cf^{252} and Cf^{254} .

The ratio of activity of the irradiated sample to that of the unirradiated sample as a function of time t after the exposure can be expressed as

$$R(t) = (N_2/N_{2S})[1 + (a_4/a_2)\exp - (\lambda_4 - \lambda_2)t],$$

where N_2 and N_{2S} are the numbers of nuclei of Cf^{252} in the irradiated and standard samples, λ_2 and λ_4 are the decay constants of Cf^{252} and Cf^{254} , and a_4 and a_2 are proportional to the neutron emission rates of the Cf^{254} and Cf^{252} present in the irradiated sample at the end of the irradiation. A least squares fit of the counting data to the expression above yielded the values

$$a_4/a_2 = (2 \pm 1) \times 10^{-3},$$

$$N_2/N_{2S} = (9.828 \pm 0.005) \times 10^{-2}.$$

The preirradiation value of N_2/N_{2S} was $(9.761 \pm 0.013) \times 10^{-2}$.

The relative production of Cf^{254} by epithermal neutrons, represented by the ratio a_4/a_2 , is about a factor of 100 less than had been predicted from a study of the neutron absorption cross sections of transuranic elements on the basis of systematics.*

Since the ratio a_4/a_2 depends primarily on the product of the capture resonance integrals of Cf^{252} and Cf^{253} , without additional information it is not possible to state which of the cross sections is responsible for the large discrepancy between the measured and predicted production of Cf^{254} . The

change in the ratio N_2/N_{2S} as a result of the irradiation, however, gives additional insight into the problem. The change in this ratio is the net result of (1) burnup of Cf^{252} by neutron absorption and (2) production of Cf^{252} by neutron absorption in whatever Cf^{250} and Cf^{251} may have been present in the sample before irradiation. An isotopic analysis of the irradiated sample was not available, but the range of isotopic compositions of similar material was given as follows: 70% Cf^{252} , 5 to 20% Cf^{250} , 5 to 12% Cf^{249} , 1 to 2% Cf^{251} , 0.1% Es^{254} , and $< 5\%$ Cm^{244} . With this composition and the values of the capture resonance integrals of Cf^{250} and Cf^{251} reported by Folger et al.** after the present work was undertaken, an upper limit of 70 b is obtained for the absorption resonance integral of Cf^{252} . This is a factor of > 20 lower than the value originally predicted by the systematics study, but consistent with the value of 42 b obtained by Folger. A recent refinement (A. Prince, private communication) of the theory also predicts 42 b.

Combining Folger's value for the capture resonance integral of Cf^{252} and the experimental value of the ratio a_4/a_2 results in the value of 14 ± 8 b for the capture resonance integral of Cf^{253} , a factor of five lower than the value originally predicted on the basis of systematics.** The uncertainty quoted does not, however, take into account the possibility that the actual isotopic composition of the sample lies outside the assumed range.

On the basis of these measurements, it may be concluded that epithermal neutron capture is not a promising way to produce Cf^{254} from Cf^{252} .

B. GORDON, E. WEINSTOCK

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Nuclear Materials Division

H. KOUTS

In March 1968 the AEC established at BNL a Technical Support Organization (TSO) to assist the Commission's Office of Safeguards and Materials Management (OSMM) in the conduct of the safeguards research and development program. The mission of safeguards is to establish methods of control that will guard against diversion of special nuclear materials without restricting the development of the peaceful uses of nuclear energy. Since the Atomic Energy Act of 1954, the AEC has been responsible for insuring that special nuclear material is used as intended to advance the welfare and security of the country. With the rapid growth of the nuclear industry, large amounts of special nuclear material will be produced in generating electric power and this material is becoming a significant article of commerce. The U.S. also assumed a commitment to assist and advise the International Atomic Energy Agency (IAEA) in formulating a system for international safeguards, particularly when IAEA safeguards are applied to signatories of the nonproliferation treaty. As a result of these developments the AEC initiated a program to strengthen the U.S. safeguards system and as part of this expanded effort, it was decided to establish a technical support organization at BNL.

The BNL TSO is now a division of the Nuclear Engineering Department called the Nuclear Materials Division. Herbert Kouts heads the Division and in addition to the permanent staff, the Division calls upon other BNL staff for part-time consultation and assistance in dealing with specific problems of safeguards.

The Division's function is to provide technical advice and guidance to the OSMM in a number of areas. These include the research and development being conducted for the Commission's program in safeguards and materials management, the identification of needs for additional research pertinent to this program, field-testing of equipment produced as a result of the research, the analysis and evaluation of data resulting from

systems studies, technical aspects of the AEC's development of standards and criteria for safeguards systems, and similar technical problems involved in modifying the safeguards program to keep pace with the domestic nuclear industry. The group also assists the AEC in efforts to encourage and support other national and international safeguards systems.

Detailed descriptions of the TSO work are generally transmitted to the OSMM as informal reports that are usually not published. However, a brief discussion of the tasks assigned to the group is given below.

STUDY OF THE STRATEGIC POINT CONCEPT OF SAFEGUARDS

The strategic point concept is a recent approach to the specific application of safeguards to nuclear facilities. TSO has studied this approach to provide a basis for comparison with the material balance concept currently employed in the United States. Both methods involve measurement of the materials flowing into and out of a plant or part of a plant in order to assure that all material is accounted for.

As research and application of different methods continue, the philosophies and techniques become more clearly defined. It will be necessary to compare different systems on the basis of cost-effectiveness, credibility, and political acceptability. Further discussion and analysis will be required to develop a universally acceptable approach to the roles of physical containment and surveillance activities.

H. Kouts

REVIEW OF RESEARCH AND DEVELOPMENT, PROJECTS AND PROPOSALS

OSMM has in progress and will have in the future many safeguards research and development projects. The staff of OSMM maintains close contact with these projects. The TSO is used to pro-

vide independent evaluation of such projects, to assist in assuring a coordinated pattern of research, and to assist in optimizing research and development spending.

TSO has collected information on research and development that may be of interest for safeguards purposes, and has begun to exchange such information with the U.S. Arms Control and Disarmament Agency, the International Atomic Energy Agency, and institutions in other nations which have active safeguards programs. TSO personnel have visited contractors supported by OSMM, as well as a number of other institutions which have projects of interest. On the basis of these discussions and an evaluation of the current status of instrumentation and data handling in the United States, recommendations have been prepared for research and development to be conducted in the next few years, with special emphasis on techniques and experiments which promise early results.

OSMM receives many proposals for research and development related to safeguards. These proposals are reviewed by the OSMM staff. Where appropriate, they are also reviewed by TSO for technical feasibility and relative importance to the safeguards program, and to determine whether the level of effort on the proposed program is likely to obtain the desired results within a reasonable period of time.

W. HIGINBOTHAM,
H. KOUTS, C. SASTRE, S. SUDA

CATEGORIES OF SPECIAL NUCLEAR MATERIAL SURVEY

Much of the research funded by the OSMM is directed toward the development of new inventory measurement techniques. A survey of special nuclear materials being processed in the industry was made to supply a basis for guidance in such research. The survey included visits to several typical nuclear facilities. Information was sought as to the form, composition, and availability for inventory purposes of these materials. It was found that the materials could be grouped into several broad categories, on the basis of similar analytical problems presented in measurements made on them.

Basically the inventory of any plant handling nuclear material can be broken down into three classes: product, recycle material, and reject material. In order to describe special nuclear materials in all facilities within the industry (reactors, isotope separation plants, fuel element fabrication,

reprocessing plants), six different categories of material can be used: (1) product – homogeneous and heterogeneous; (2) recycle – noncontract specification material and easily recovered scrap; (3) reject – difficult to recover scrap and noneconomic scrap.

In addition, current industry practices have led to some similarities in packaging which in turn permit certain generalizations to be made with respect to containers. On the basis of the characteristics of the broad categories of material and the generalizations that can be made about containers, potential areas for the use of nondestructive techniques for inventory measurements have been indicated.

A. COURT, K. DOWNES

INSTRUMENTATION FOR NONDESTRUCTIVE ASSAY

The sodium iodide scintillation detectors and single channel analyzers now used by the U.S. and the IAEA inspectors were evaluated. A number of samples of uranium and plutonium were analyzed using high-resolution germanium detectors and multichannel analyzers. In cooperation with the Arms Control and Disarmament Agency, several portable instruments for passive analysis are being procured for evaluation in the field. One such instrument was built by the BNL Instrumentation Division. Information has been collected from a number of institutions on the latest techniques in high-resolution γ -ray spectroscopy and passive methods of measurement using neutrons. These may be useful for national and international inspectors, or in field tests of safeguards systems.

W. HIGINBOTHAM, C. SASTRE

SEALS FOR SAFEGUARDS

A study of the role of security seals as safeguards has started. This task involves two separate activities, testing the seals and determining where they should be used.

Seals of the type used by the IAEA and by the Internal Revenue Service are being tested to determine how they might be opened and reclosed without leaving evidence of tampering that is detectable by the post-mortem examination used by the IAEA. This testing is expected to result in recommendations on improvements in design of the seals and on identification techniques. In this phase of the program, testing is arbitrarily limited

to forms of attack that do not involve disguising cuts or perforations. The use of magnetic fields has been considered, and some exploratory tests have been performed.

A system-oriented analysis of sealing operations has started, with a view to identifying the areas of applicability of seals and their limitations. Alarm devices and attack-resistant volumes are included.

A survey has been made of commercially available seals, and contacts have been established through visits with various groups active in the development and testing of seals. C. SASTRE

SPECIAL ANALYTICAL STUDY OF SAFEGUARDS

The TSO assisted the OSMM in a study for the AEC and the Bureau of the Budget that described the safeguards problem as it appears today, and it indicated in general terms the measures that the AEC is likely to take in developing safeguards for the domestic nuclear industry and for international areas. W. HIGINBOTHAM, H. KOUTS

U.S. SAFEGUARDS SYSTEM DEFINITION AND DESCRIPTION

TSO has been collecting information on the present U.S. safeguards system in order to relate the research and development program to the current needs. The systems analyses discussed below will also contribute to this objective. The outcome of these studies will be embodied in a report which describes the present and projected U.S. safeguards program in a comprehensive manner. S. SUDA

PARAMETRIC ANALYSIS OF NUCLEAR PROCESS MODELS

Nuclear process models are being developed at the National Bureau of Standards and Battelle Northwest Laboratory. These systems studies are to be used to analyze the effectiveness of safeguards and their cost and obtrusiveness. These mathematical studies should provide (1) a basis for choice of safeguards techniques, (2) guidance for field tests, (3) direction for evolution of present U.S. systems, and (4) guidance on research and development.

Information on the general characteristics of processes and equipment currently in use in the

Figure 1. Annual costs for safeguards by IAEA - alternative assumptions.

nuclear industry is being obtained in order to create a meaningful mock-up of a typical facility. In this connection members of the group are cooperating with safeguards studies at other laboratories. K. DOWNES, A. COURT, S. SUDA

IAEA STAFFING FOR SAFEGUARDS UNDER THE NONPROLIFERATION TREATY

The first report written under this heading was presented by the AEC to the Committee on Foreign Relations of the U.S. Senate.* This report provided a forecast of the cost of IAEA safeguards for the period 1970-1990, based on straightforward extension of the current IAEA system. Figure 1 summarizes some of the findings of the report showing costs under three possible alternatives for implementing the IAEA safeguards system.

*Hearing on the nonproliferation treaty before the Committee on Foreign Relations, U.S. Senate, July 10, 11, 12, 17, 1968, pp. 153-155, 281-288.

The requirements of the IAEA system in cost and manpower are clearly of interest to all participating nations. TSO will continue to review revisions to estimates on the growth of the nuclear industry and the effects on staffing and costs of safeguards, in cooperation with all other interested parties.

R. EDWARDS, W. HIGINBOTHAM,
H. KOUTS, L. GREEN

GLOSSARY OF TERMS

A glossary is being prepared of the special terms currently being used in the nuclear safeguards field. Definitions are being collected from many sources, and they are edited and rewritten where necessary. A data file of this information is stored on IBM cards for sorting. Current printouts have been circulated for comments to interested parties within the U.S. and abroad. At present, the glossary is a collection of current usage (good and

bad); in the future it is planned to compile a list of recommended terms and definitions. F. MILES

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National Neutron Cross Section Center

S. PEARLSTEIN

ADVISORY COMMITTEE

An Advisory Committee was appointed by the Nuclear Engineering Department to review the activities of the National Neutron Cross Section Center (NNCSC). The members of this committee are R. Ehrlich (Knolls Atomic Power Laboratory), H. Goldstein (Columbia University), P. Greebler (General Electric - Atomic Products Operation), G.C. Hanna (Atomic Energy of Canada Ltd., Chalk River), R. Lazarus (Los Alamos Scientific Laboratory), and A.B. Smith (Argonne National Laboratory).

The first meeting of the Committee with NNCSC personnel took place November 28-29, 1967, at which time a statement of NNCSC objectives and priorities was presented and discussed. The second meeting, held April 29, 1968, was devoted primarily to the discussion of SCISRS-I status and SCISRS-II development.

EXPERIMENTAL NEUTRON DATA LIBRARY

All of the energy-dependent data and resonance parameters from the old Sigma Center files have been prepared for insertion into the SCISRS library. Only thermal cross section values remain to be completed.

Efforts to detail the "content" of the SCISRS-II system (a new data storage and retrieval system) began. Assistance was obtained from experimental and evaluation groups in ascertaining what is necessary and what is useful to make the new library an appropriate tool for all users. Input format problems were investigated in collaboration with the NNCSC programmers and personnel from both the ENEA and IAEA data centers.

EVALUATED NUCLEAR DATA FILE

The first version of the ENDF/B library was distributed to cross section users in the United States and Canada and to member countries of the European Nuclear Energy Agency. The ENDF/B library was assembled in a cooperative program

among USAEC-supported laboratories to increase the amount of completed data sets available to reactor designers. These tasks are performed by the Cross Section Evaluation Working Group (CSEWG). Meetings of the CSEWG took place at BNL on January 16-17, 1968, and September 16-18, 1968. In addition to cross section evaluation the meetings were devoted to defining ground rules for testing data, defining the criteria for re-evaluation of data, and conducting seminars and workshops on special topics.

COMPUTER APPLICATIONS

The programs DAMMET (code to delete, alter mode, and merge tapes) and CHECKER (code to detect errors in data preparation) were extended to improve their versatility and operating performance. Development is continuing on the PLOTFB (code to read, write, and plot data) program in order to allow all neutron data included in the files to be processed. In addition, the codes DAMMET, CHECKER, and PLOTFB are being extended to include the data in the newly proposed photon files.

A new data storage and retrieval system was developed to replace SCISRS; this system has been tentatively named SCISRS II. The main characteristic of the new system is that bibliographic and numeric information will be stored separately, and the system format will be expandable to include a wide variation of data. An elemental version of the system now exists. This program will retrieve data based on criteria such as Z , A , reaction type, data type, and energy range.

The initial retrieval package for SCISRS II, which is now in operation on the CDC 6600, is being debugged for operation on both the IBM 7094 and IBM 360/30 (Administrative Data Processing machine). A program is currently under development to allow input to SCISRS II to be in the original SCISRS card input format. Once this program is completed, work will commence on a program to allow SCISRS II to accept data in the ECSIL (system for storage, retrieval, and display of experimental

neutron data—Lawrence Radiation Laboratory, Livermore) format.

The ECSIL system is at present in a late stage of implementation on the IBM 7094. In order to minimize development time, not only the ECSIL program but actually the entire Livermore operating system is being employed. This procedure will allow complete compatibility with the system as it now exists at Livermore.

NNCSC COMPUTER

A study of the computation needs of the NNCSC strongly indicates the need for a computer that can be devoted largely to data file manipulation. Bids from several manufacturers have been received in response to specifications issued by BNL, and an evaluation of the proposals is in progress.

Figure 1. $\langle E_k \rangle$ vs $(19 + \epsilon - E_f) \times A^{2/3}$.

Figure 2. $\bar{\nu}_p$ vs $\langle E_k \rangle$.

AUTOMATED PUBLICATION

Progress was made in an effort to find a way to treat angular distribution data, taken directly from the SCISRS library, in such a manner that usable computer-based plots could be obtained, including curves through the data points. Studies are continuing on ways to reduce the human interaction with the process, which is still large.

AVERAGE NEUTRON YIELD FROM FISSION

A revised version of earlier work [see BNL 50082 (S-70), p. 20] concerned with estimation of thermal capture and fission cross sections and resonance integrals was completed. The intent of this work was to establish a systematic procedure for estimating fission and capture thermal cross sections and fission and capture resonance integrals for transuranium isotopes. The method involved establishing a correlation between the difference of the binding energies, fission thresholds, cross sections, and resonance integrals. The method of analysis was improved and extended to include $\bar{\nu}_p$ (average number of prompt neutrons) and $\langle E_k \rangle$ (average kinetic energy of fission fragments).

This investigation correlated the average kinetic energy of the fission fragments $\langle E_k \rangle$ and the average prompt neutron yield $\bar{\nu}_p$. These relationships are given in Eqs. (1) and (2) and are depicted in Figures 1 and 2.

$$\langle E_k \rangle = -406.4242 + 1.9531774\varphi - 0.001594435\varphi^2 + \epsilon \text{ (MeV)} \quad (1)$$

where

$$\varphi = A^{2/3} (19.0 + \epsilon - E_f),$$

A = mass of fissioning nucleus,

E_f = effective fission threshold,

$$\epsilon = \begin{cases} 0.0 & \text{for even-even} \\ 0.5 & \text{for odd-odd} \\ -0.9 & \text{for even-odd} \end{cases} \text{ compound nucleus.}$$

$$\langle \nu_p \rangle_i = \alpha_i + \beta_i \langle E_k \rangle + \gamma_i \langle E_k \rangle^2 + \delta_i \langle E_k \rangle^3, \quad (2)$$

where $i=1,2,3$ depending upon three different values of the slope $d\nu_p/dE_n$ (E_n = neutron incident energy).

A set of third order semiempirical equations were also derived as a function of the Coulomb separation energy $Z^2/A^{1/3}$ and are graphically displayed in Figure 3.

OPTICAL MODEL CALCULATIONS

An optical model study was completed of total cross sections and elastic angular distributions for the three lead isotopes Pb^{208} , Pb^{207} , and Pb^{206} at 0.5, 1.0, and 2.5 MeV. The conventional real Saxon well, Gaussian imaginary well, and Thomas spin-orbit terms were used.

The region of good fit was found to be large at 1.0 MeV. The following sets of parameters give good fits to the experimental data at 1.0 MeV; the results for Bi^{209} are also included.

	Pb^{208}	Pb^{207}	Pb^{206}	Bi^{209}
V_{RE} (MeV)	50.0	52.0	48.0	50.0
r_0 (F)	1.20	1.175	1.25	1.20
V_{IM} (MeV)	2.0	2.0	3.0	2.0
V_{SR} (MeV)	7.0	14.0	17.0	13.0
a (F)	0.55	0.55	0.55	0.55
b (F)	1.0	1.0	1.0	1.0

At 2.5 MeV there is a region of good fit but not as large a region as that at 1.0 MeV. The best sets are:

	Pb^{208}	Pb^{207}	Pb^{206}	Bi^{209}
V_{RE} (MeV)	46.0	46.0	46.0	46.0
r_0 (F)	1.24	1.25	1.25	1.25
V_{IM} (MeV)	7.0	3.0	3.5	4.0
V_{SR} (MeV)	7.0	6.0	6.0	7.0
a (F)	0.65	0.65	0.65	0.65
b (F)	1.0	1.0	1.0	1.0

The best fits to the total cross sections and elastic angular distributions at 0.5 MeV are given most often by small radii and deep wells.

It was possible to find a common set of parameters that fits the data for Bi^{209} at the three ener-

gies. This involved changing the V_{IM} in the 2.5-MeV set from 4.0 to 3.6 MeV.

The work was started in 1965 by the late R.B. Day of Los Alamos Scientific Laboratory. The data, except for those for Bi^{209} at 2.5 MeV, were his. Although he saw the direction in which the work was going, he did not see the final results.

Optical model calculations were carried out on Co^{59} for energies from 0.1 to 4 MeV. Comparison of $\sigma_{n,\gamma}$, σ_{el} , σ_{T} , and $d\sigma_{\text{el}}/d\Omega$ with experimental data was very satisfactory.

An optical model analysis of the scattering and reaction cross sections for Cf^{252} was completed for neutron energies ranging from 1 keV to 15 MeV.

The coupled-channel code JUPITER I was modified to generate transmission coefficients corresponding to both spherical and nonspherical potentials. The generalized transmission coefficients for the coupled-channel analysis are punched automatically and are in the format required by NEARREX to calculate compound elastic, inelastic, capture, and fission cross sections.

RESONANCE REGION CALCULATIONS

A study of the resolved resonance region of Co^{59} was initiated. To date the work has shown that while one bound level is needed to match the thermal capture data, two bound levels, one for each s -wave spin state, are needed to satisfy polarization data.

Previously reported calculations [T.E. STEPHENSON AND A.M. FERRER, Total neutron cross section of holmium below 235 eV. (A) *Bull. Am. Phys. Soc.* 12, 650 (1967)] for holmium were extended. Resonance parameters for 76 resonances of Ho below 500 eV, selected from the literature and from values compiled and recommended in BNL 325, were used as the starting point in fitting the total neutron cross section data to a Breit-Wigner multi-level scattering and single-level absorption formula. The addition of two bound levels, one for each s -wave spin state, yielded a calculated ratio of thermal neutron capture cross sections for the two spin states which agreed with experiment ($\approx 60\%$ for $J = 3$), as did the calculated value of the thermal capture cross section, 67 b. In addition, the two bound levels enabled 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 were also calculated (≈ 672 and 125 b, respectively).

Figure 3. $\bar{v}_p$ vs $Z^2/A^{1/3}$.

A corrected version of the program MLBW (K. GREGSON, M.F. JAMES, AND D.S. NORTON, UKAEA Report AEEW-M517, 1965) was adapted to read in the resolved resonance parameters from File 2 of ENDF/B and to calculate scattering, capture, and fission cross sections. The scattering cross section could be calculated either as a sum of single-level Breit-Wigner terms or by using a multilevel formula which allows for level-level interference. This program, SIGPLOT, was further modified to include corrections for Doppler broadening.

A program, AVERAGE, was written to calculate average scattering, capture, and fission cross sections in the 1 to 100-keV region from the data read directly from ENDF/B.

Formats were set up for storing multilevel resonance parameters on the ENDF/B tapes. These formats were specifically designed for the Reich-Moore and Adler-Adler formalisms. The programs COMBICO (Reich-Moore) and CODILLI (Adler-Adler) are being evaluated; while they are now operable at BNL, it appears that modifications are desirable before recommending them as reference programs for the CSEWG.

A program, SIGTEST, was written and debugged for making a nonlinear least-squares fit to cross-section data using the Adler-Adler formalism. Cross sections were calculated as a function of energy with an initial set of parameters, Doppler-broadened using ψ and χ functions, and fitted to the experimental data. The effect of resonances outside the energy range of experimental points was taken into account, and as many as 25 resonances could be fitted in the energy range covered by the experimental points. This program is now being used to fit fission cross section data of Pu^{239} .

NUCLEAR REACTION THEORY

The influence of direct reactions on cross-section distributions in the continuum region is being investigated numerically with the help of random matrix techniques. The results will be compared with those of the older Ericson method.

An effort is being made to derive an analytical expression for the two-angle distribution law corresponding to the F_2 -ensemble of unitary matrices. The single-angle distribution law was derived previously.

The polarization studies in the continuum region originally limited to incident spin- $\frac{1}{2}$ polarized nuclei were extended to include incident polarized

nuclei of any spin, provided spin tensor moments of higher order vanish. The methods were also applied to the calculation of the average polarization induced by the scattering of unpolarized nuclei.

The application of random matrix theory to systems not completely random is being investigated. One important consequence of the assumption of incomplete randomness is the appearance of a double peak in the energy level spacing distribution, an effect which has been observed experimentally [J.B. GARG ET AL., *Phys. Rev.* **134**, B985 (1964)]. M. GOLDBERG, M. BHAT, D. CULLEN, T. KRIEGER, W. KROPP, B. MAGURNO, V. MAY, S. MOORE, S. MUGHABGHAB, S. PEARLSTEIN, 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 over-all 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. The report assessing the role of thorium was circulated by the AEC to interested groups in industry and the national laboratories for comments prior to its formal issuance.

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. The final draft report was reviewed by BNL personnel and comments submitted to the AEC.

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, as well as of a special working group to help in writing the final report. Assistance was rendered in writing several sections of the final report, in evaluating the linear program output, and in devising ways of presenting the data. More than 100 graphs were prepared for inclusion in the report encompassing each case investigated. Included were 38 composites consisting of a table and bar graph of the new reactors to be built in each two-year period and a graph of the total power generated by each reactor system with time for each case, 35 graphs showing the capital cost and annual cost reductions required to permit each reactor type to enter the economy in each two-year period, and 3 graphs showing the characteristics of each reactor considered for the system, i.e., specific power, yield, ore and separative work requirements, and levelized energy costs.

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

EVALUATION STUDIES

Reports in four major areas of interest were evaluated for the AEC or its contractors. At the request of the AEC's RDT, cognizant individuals at BNL evaluated additional drafts of the 10-year program plans leading to the introduction of a liquid-metal-cooled fast breeder reactor (LMFBR). These drafts were prepared by the LMFBR Program Office at Argonne National Laboratory. Sections 1 (Over-all Plan), 2 (Plant Design), and 7 (Fuels and Materials) were reviewed in this period and the comments forwarded to ANL. The other sections were reviewed previously.

BNL is participating in the development of codes and standards applicable in the reactor

field. This is part of an AEC-sponsored program at ORNL and the Atomic International Liquid Metal Engineering Center (LMEC). The ORNL work involves the consolidation of current power technology and engineering practices and the development of basic standards for AEC-owned water reactors. This work will also help define the existing technological base upon which advanced development programs will be built. A similar effort at the LMEC involves standards applicable to the LMFBR program. Detailed comments on some 52 standards have been submitted thus far. BNL is also represented on subcommittees of the USASI-NSB (USA Standards Institute, Nuclear Standards Board) Standards Committee N-101.

The *Guide for Economic Evaluation of Nuclear Reactor Plant Designs* was reviewed for ORNL. This report was prepared by Nuclear Utilities Services, Inc. (NUS) as a revision of the 1962 *Nuclear Cost Guide*. It was felt that NUS very ably condensed a large amount of information into a single concise volume. The methods outlined for calculating

and listing costs and their components are consistent with procedures that have been developed over the last six years. The report presents a high degree of sophistication used in current reactor evaluations.

BNL supplied evaluated technical and economic data on the Molten Salt Breeder Reactor to the AEC for transmittal to the joint India-USA Study Group.

L. EPEL, C. RASEMAN,
H. SUSSKIND

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Chemistry Division

R.H. WISWALL, JR.

High Temperature Chemistry

SPECTRA OF MOLTEN SALTS

At the present time considerable controversy surrounds the interpretation of the vibrational spectra of fused salts. Thus, many investigators believe the data support the existence of associated or "complex" entities and, in fact, often postulate the simultaneous coexistence of four or more "complexes" to explain their observed spectra [R.B. ELLIS, *J. Electrochem. Soc.* **113**, 485 (1966)], while other workers prefer to interpret the spectra more in terms of extended latticelike vibrational modes [J.K. WILMSHURST, *J. Chem. Phys.* **39**, 2545 (1963)]. In an attempt to clarify this situation an investigation has been undertaken of the inelastic scattering of cold neutrons from fused salts with the use of the slow chopper facility at the BGRR. Until this reactor was placed on standby last June, inelastic scattering data had been recorded at two angles of scattering for molten zinc chloride, potassium chloride, and their 1:1 binary mixture, and at one angle of scattering for the mixtures $\text{ZnCl}_2:2\text{KCl}$ and $\text{KCl}:2\text{ZnCl}_2$.

The neutron scattering data, although incomplete, do indicate the existence of definite dispersion relations for the phonon modes in these melts. In the case of zinc chloride, the neutron data correlate well with the available infrared [J.K. WILMSHURST, *J. Chem. Phys.* **39**, 1779 (1963)] and Raman results [E. J. SALSTROM AND L. HARRIS, *J. Chem. Phys.* **3**, 241 (1935)], and support an interpretation of the spectral data in terms of a quasi lattice having a repetitive three atom "primitive cell," the six optical modes being assigned in terms of an infrared and Raman active doubly degenerate transverse mode at 284 cm^{-1} , a Raman active longitudinal mode at $\approx 350\text{ cm}^{-1}$, and a Raman active triply degenerate mode at 228 cm^{-1} . The dispersion of the longitudinal acoustic mode provides a tentative estimate of the sound velocity in zinc chloride at 400°C as 535 sec^{-1} , somewhat

lower than the ultrasonically determined [G.J. GRUBER AND T.A. LITOVITZ, *J. Chem. Phys.* **40**, 13 (1964)] value of $971\text{ meters sec}^{-1}$, and also provides an estimate of the chlorine-chlorine distance between neighboring "primitive cells" as $3.8\text{ \AA}$.

J. WILMSHURST, J. BRACKER

DOUBLE LAYER CAPACITANCE IN MOLTEN SALTS

Measurements on the properties of the double layer in molten salts are needed for (1) an understanding of electrode processes and electrode kinetics in these systems, (2) a more basic understanding of practical topics such as electrocrystallization, and (3) obtaining data for constructing a model of the double layer. Work has therefore continued on the measurement of double layer capacitance as reported in the last annual progress report.

Several changes have been made in the apparatus and a diagram of the latest cell is shown in Figure 1. This incorporates a Pb-PbCl_2 (10% by weight in LiCl-KCl eutectic) reference electrode. A molten lead dropping electrode has also been used in addition to the previously reported molten bismuth. More care has been used to purify the salts.

The capacitance curves obtained with lead and bismuth in LiCl-KCl eutectic are shown in Figure 2. These curves were measured at a frequency of 5 kHz but the value of the capacitance did not change $>3\%$ by varying the frequency between 1 and 20 kHz. The curves show results for lead at 390° and 480°C with very little change in capacitance with temperature. A second curve of Pb at 390°C is given to show the precision between different experiments. The results of Ukshe et al. [*Electrochim. Acta* **9**, 431 (1964)] on lead in a LiCl-KCl (1:1) mixture are shown for comparison. The shape of the curve is similar to that obtained in this work but there is some discrepancy in the magnitude of the capacitance. Also these authors report a temperature coefficient of capacitance of

Figure 1. Diagram of improved cell used for capacitance measurements at metal-salt interfaces.

+ 5 $\mu\text{fd}/100^\circ\text{C}$, a result which has not been confirmed in the present measurements.

It is believed that the use of dropping electrodes in high temperature systems has been useful for capacitance measurements as shown by the elimination of frequency dispersion. Further work is necessary on the purification of the salts used (a small current of $\approx 1 \mu\text{A}$ always flowed through the salt during our measurements). Work is under way to extend these measurements to 800°C so that pure salts instead of mixtures can be examined. A quartz capillary has been successfully tested for this purpose.

J. EGAN, R. HEUS

Figure 2. Capacitance of dropping liquid metal electrodes in fused salts as a function of potential.

HALOGEN-METAL HALIDE SOLUTIONS

The study of the solution chemistry of halogen gases dissolved in their respective halides reported in the previous report [BNL 50082 (S-70)] was continued. It was found that chlorine entered the pores of a dense graphite electrode (density 1.9) rendering this electrode useless for obtaining cathodic chronopotentiograms of chlorine dissolved in molten chloride. Two nonporous forms of carbon were tested as possible electrode materials, pyrolytic graphite and a vitreous carbon (produced by Beckwith Carbon Corp.). Pyrolytic graphite blades were used as an electrode but fabrication problems were encountered. A satisfactory cathode material was found in the vitreous carbon. This material is impermeable to gases, resists attack by chlorine at the temperatures studied, has a smooth finish, and has a coefficient of thermal expansion matched by some Pyrex glass. Vitreous carbon to Pyrex seals were made leak tight and were compatible with the molten chloride systems studied.

Cathodic chronopotentiograms were obtained for chlorine dissolved in molten lead chloride, silver chloride, and the lithium chloride-potassium chloride eutectic. Figure 3 shows the chronopotentiometric cell used. From the basic equation of chronopotentiometry,

$$i_0\tau^{1/2} = (nF\pi^{1/2}D^{1/2}C)/2,$$

diffusion coefficients of chlorine dissolved in molten chlorides were calculated; Table 1 gives the results obtained.

Figure 3. Chronopotentiometric cell.

The values obtained for the diffusion coefficients are larger by an order of magnitude than those usually found for ions in molten salts ($\approx 10^{-5}$ cm²/sec), but agree with results for chlorine in other molten chloride systems reported in the literature.

The solubility of bromine dissolved in molten bromides was measured as a function of temperature, and the heats of solution were calculated (Table 2). These results are tentative and will be checked further. The solubility of bromine in molten bromides is an order of magnitude greater than those for the comparable chlorine-molten chloride systems [see BNL 50082 (S-70)], and the heats of solution are negative indicating a stronger

Table 1

Diffusion Coefficients of Chlorine in Molten Chlorides

Salt	Temperature, °C	$D \times 10^4$ cm ² /sec
LiCl-KCl eutectic	400	0.60
	450	1.6
	500	1.7
	550	1.5
PbCl ₂	580	3.5
AgCl	518	3.7

Table 2

Solubility of Bromine in Molten Bromides

Salt	Temperature, °C	Solubility, moles/cc $\times 10^6$	Solubility, mole fraction $\times 10^5$	$\Delta \bar{H}^\circ$, kcal/mole
PbBr ₂	430	1.39	9.21	-1.3
	519	1.23	8.32	
LiBr	617	1.75	6.1	-9.5
	709	1.04	3.7	

interaction with the bromide melts than with the comparable chlorine-chloride systems.

J. VAN NORMAN, R. TIVERS

Physical Organic Chemistry

RADIOLYSIS OF FLUOROCARBONS AT ELEVATED TEMPERATURE

Perfluoroaromatics

The effect of temperature on the radiolysis of hydrocarbon polyphenyls has been widely studied in the last few years in connection with their application as reactor coolants. It is known that, in general, they show only a small increase in decomposition rate with temperature up to about 350°C. Above this temperature region, their radiolytic decomposition rates increase quite rapidly. Arrhenius plots yield activation energies for over-all decomposition of ≤ 1 kcal/mole in the lower temperature region, and of the order of 20 kcal/mole in the higher.

From our work with aromatic fluorocarbons it appears that perfluorobiphenyl shows similar behavior (Figure 4), although the temperature of

transition between the lower and higher activation energy regions is above 450°C (at least 100° higher than for the hydrocarbons). Perfluorobenzene, perfluoronaphthalene, and perfluoro-*o*-terphenyl probably also behave similarly, but have been studied only up to 450°; at this point they have either not yet, or only just, entered the region of higher activation energy.

In the lower temperature region (below 450°), although G -values for over-all decomposition do not change much, there is a rather large change in the product distribution. This is particularly evident in the case of C_6F_6 whose radiolysis product yields at ambient temperature and at 450° are

Figure 4. Arrhenius plot of perfluorobiphenyl radiolysis results. The apparent activation energy in the lower temperature region is 0.5 kcal/mole. A value cannot be determined for the high temperature region without more points. The slope of the dotted line (probably a minimum) gives a value of 5 kcal/mole.

listed in Table 3. For one thing the yield of perfluoro-cyclohexadienes (C_6F_8) increases by a factor of 10 in going from ambient to 450°. The polymeric products also change markedly. At the lower temperature, >90% of the polymer is a product of relatively high molecular weight and only about 2% is the dimer, perfluorobiphenyl. At 450°, however, 60% is dimeric, made up of 20% partially saturated dimers and 40% perfluorobiphenyl. The marked increase in yield of dimers is accompanied by a significant decrease in absolute yield of higher polymer. This situation is not simply explained (e.g., in terms of positive and negative temperature coefficients). A plausible mechanism has been developed to account for these results and is discussed in some detail in a paper accepted for publication in *J. Phys. Chem.*

Perfluorobicyclohexyl

The compound $C_{12}F_{22}$, perfluorobicyclohexyl, was shown in earlier work [BNL 50082 (S-70)] to be uniquely (for fluorocarbons) unstable toward thermal decomposition. Scouting experiments had also indicated great sensitivity to radiation at high temperatures [BNL 954 (S-68)]. In current work, an attempt has been made to get quantitative information on the combined effects of radiolysis and pyrolysis. In analyzing the data, some assumption must be made about the interaction of the effects. The simplest is that of additivity, i.e., that meaningful G -values can be calculated by subtracting from the total decomposition the amount of pyrolytic decomposition that occurred in a separate experiment without radiation. This assumption is of course of dubious validity.

Two series of radiolysis and parallel pyrolysis experiments were carried out, one at relatively low pressures of 1 to 2 atm and the other at pres-

Table 3

Effect of Temperature on Product Distribution in Radiolysis of C_6F_6

Temperature, °C	Dose, Mrad	$G_{-C_6F_6}$	G -values in terms of loss of C_6F_6				
			C_6F_8	Total polymer	$C_{12}F_{10}$	Partially saturated dimers	Higher polymer
67	107	3.0	≈ 0.04	2.9	≈ 0.05	0.15 ^a	2.7
450	78	6.3	0.4	5.9	2.3	1.2 ^a	2.4

^a Assuming same GLC detector sensitivity as for $C_{12}F_{10}$.

tures greater than critical. In the low pressure series G -values, calculated on the additivity assumption, increased somewhat >10 as the temperature increased from 350° to 400° , then appeared to decrease again and actually to become negative at 415° . Pyrolytic decomposition was too severe to go to higher temperatures. At the high pressures, pyrolysis was not so severe, and apparent G -values increased at $>415^\circ$. They did not become negative at 415° , but the ratio of "radiolytic" to "pyrolytic" damage did go through a minimum at this temperature. Also at temperatures $\geq 415^\circ\text{C}$, the extent of "radiolytic" decomposition changed very little with dose over several orders of magnitude, which meant that apparent G -values varied to the same extent. It was not possible at temperatures $>400^\circ$ to irradiate the $\text{C}_{12}\text{F}_{22}$ at a high enough dose rate to produce more "radiolytic" decomposition than "pyrolytic." Thus it appears that pyrolysis is the more important process at these temperatures. While the results cannot be explained in detail yet, it is likely that a thermal, rather than radiolytic, chain reaction is operating at all temperatures, particularly the higher ones, and that this chain is fed by radicals formed by radiation. Ionic reactions, possibly even chains, may be significant, but apparently are not responsible for the bulk of the reaction. D. MACKENZIE, F. BLOCH,

W. RIEL, R. SMOL, V. WILSON

FLUOROCARBON REACTION MECHANISMS

Studies of the role of valence isomers in radiation chemistry were continued. G -values for the formation of Dewar hexafluorobenzene and Dewar decafluoroxylene from their respective aromatic parents were determined as 0.02 and 0.05/100 eV. Dewar C_6F_6 , besides reverting to its Kekule form, polymerizes with $G \approx 20$. Valence isomers have now been observed in the γ radiolysis of hydrocarbon benzene (Wilzbach and Kaplan, ANL) and are thus common in the radiolysis of benzenoid aromatic systems. These results further support our proposed "energy sink," whereby part of the energy absorbed by an aromatic system under radiolysis is stored in the form of long-lived interconvertible valence isomers. These in turn can react further to yield polymers or decay to the ground state.

Radicals of perfluorobiphenyl, -benzene, and -naphthalene which cannot be prepared directly by chemical reaction have been prepared by γ ir-

radiation in frozen glassy matrices. Mixtures of cyclic and straight chain fluorocarbons were found to form stable glasses at 77°K and could be used to trap these radicals. J. FAJER, R. SMOL

PORPHYRINS

The oxidation-reduction properties of porphyrins play a key role in their biological function in respiration and photosynthesis. The work described here represents an attempt to clarify these properties. Cation radicals of various porphyrins and of ethyl chlorophyllide a , as well as several dications, have been prepared by chemical and electrochemical oxidation.

Electrolysis of magnesium octaethylporphyrin (MgOEP) in CH_2Cl_2 at $+0.7\text{ V}$ vs SCE (aq.) yielded a blue-green solution, and the resultant species (principal absorption maximum at 378, 392, 585, and 660 nm, see Figure 5) was shown by coulometry to be the product of a one-electron oxidation. Isosbestic points, observed as the oxidation was followed spectrophotometrically, were indicative of the smooth course of the reaction. ESR measurements on these solutions showed a single line, $g = 2.0028$ and 2.5 gauss wide (peak to peak). MgOEP underwent a similar one-electron oxidation when treated with bromine in either methylene chloride or chloroform. The product of the chemical oxidation was spectroscopically similar to the cation radical obtained via electrolysis and was stable in these solvents.

Open-shell, restricted Hartree-Fock calculations of the optical and esr spectra of the porphyrin cation radical were performed in the Pariser-Parr-

Figure 5. Absorption spectra of MgOEP (—), MgOEP⁺ (---), and MgOEP²⁺ (- - -) in CH_2Cl_2 .

Pople approximation. Calculated transitions are at 371, 398, 724, and 740 nm. In the same order, dipole oscillator strengths are 0.032, 1.628, 1.014, and 0.018.

Additional evidence for simple cation radicals is found in the reversible one-electron oxidation of magnesium, cadmium, and zinc tetraphenylporphyrins (TPP). Thus the partially resolved 9-line esr spectrum of ZnTPP⁺ (Figure 6, second derivative presentation) can readily be assigned to four equivalent nitrogens. Hyperfine splitting constants of $a_N = 1.5$ and $a_H = 0.25$ g (eight β protons of the pyrroles) were obtained by the SCF-MO calculations. A computer-simulated spectrum (Figure 6), based on $a_N = 1.43$ and $a_H = 0.24$ g, adequately resembles the experimental data.

Continued electrolysis of MgOEP⁺ at +0.9 V vs SCE resulted in the removal of an additional electron, and the optical spectrum at this stage is shown in Figure 5. (The esr signal associated with MgOEP⁺ decreased during the course of the electrolysis.) Two-electron reduction of this new species regenerated 95% of the initial MgOEP. Addition of MgOEP to the oxidized product reformed the cation radical in accord with the reaction:

Figure 6. (a) Second derivative esr spectrum of ZnTPP⁺ in CH₂Cl₂. (b) Computer simulated spectrum: 1.22 g linewidth, Lorentzian line shape, 4 equiv. nitrogens, $a_N = 1.43$ g, and 8 equiv. protons, $a_H = 0.24$ g.

Figure 7. Absorption spectra of CoOEP (—), [Co(III)OEP]⁺+Br⁻ (---), and [Co(III)OEP]⁺+2Br⁻ (····) in CHCl₃.

Figure 8. Absorption spectra of ethylchlorophyllide *a* (—) and its cation radical (---) in CH₂Cl₂.

Electrolysis of MgTPP⁺ and ZnTPP⁺ also proceeded to the dication stage. Oxidation of metalloporphyrins, by the methods described, is not limited to group II metals but may be extended to transition metals. Thus Co(II) octaethylporphyrin [Co(II)OEP] in chloroform underwent two distinct one-electron oxidations when treated with bromine. The first step, which required 0.51 ± 0.02 mole of bromine, brought about the oxidation of divalent to trivalent cobalt giving [Co(III)OEP]⁺+Br⁻. Further oxidation of the trivalent complex used 0.51 ± 0.02 mole of bromine and yielded a green species (Figure 7) formulated as [Co(III)OEP]⁺+2Br⁻. This formulation is supported by the quantitative conversion of the dication according to the following reaction:

The two-electron oxidation stage could also be reached by electrolysis in CH₂Cl₂.

One-electron oxidation of ethyl chlorophyllide *a* at 0.6 V vs SCE yielded a yellow solution whose optical spectrum is shown in Figure 8. The product exhibited a singlet esr signal 9 gauss wide (peak to peak). (Attempted chemical oxidation by bromine led to allomerised material.) This species may be related to radicals observed in photosynthesis.

Stable oxidized products of CoTPP, H₂TPP, zinc tetraphenylchlorin, free base and zinc etio-porphyrin I, and ZnOEP have also been prepared by the above techniques. J. FAJER, D. DOLPHIN,* R. FELTON,** D. BORG†

Graphite Chemistry

The reaction of graphite and hydrogen has been studied at temperatures above 3000°K to determine the mechanism of formation and the reaction products. This has been shown to be a vapor phase reaction, involving the vaporization of graphite and subsequent reaction with H₂. Emphasis in the past year has been placed on investigation of the behavior of graphite from 2500° to 3500°K. This has been done using our filament technique, previously described, to determine the rate and heat of vaporization of graphite, and spectroscopy to investigate the carbon species formed.

Acetylene is a primary product of the vapor phase reaction of graphite and H₂ at low pressure, and will be produced when small particles of graphite or carbon are heated by collision of fission fragments or alpha particles. The results of this work can be used to predict the product composition and the energy balance in that case. In summary, it has been found that (1) C₂ is probably the most prevalent species in "free" evaporation from graphite, (2) disappearing filament and photoelectric pyrometer temperature readings with the use of graphite in inert gases above 3000°K are in error as a result of soot formation, and (3) active species can be stabilized by condensing vaporized graphite at liquid nitrogen temperatures.

The rate of vaporization of graphite in vacuum was measured from 2400° to 3400°K and the results are shown in Figure 9. These results were ob-

tained by resistively heating a flat graphite filament for a precisely controlled length of time. At temperatures below 3000°K, the temperature measurements were made simultaneously with a disappearing filament and a photoelectric pyrometer. Above 3200°K, the temperature had to be obtained by the photoelectric pyrometer.

Treating the data of Figure 9 by the second law of thermodynamics, one finds that the heat of vaporization of graphite is 210 ± 10 kcal/mole; this assumes the vapor species are in equilibrium. Spectroscopic investigation of C₂ evaporation indicated that it equilibrated in heating times less than those used in these experiments.

The data of Figure 9 were also analyzed using third law calculations and published spectroscopic data. The carbon vapor pressure was calculated using the Langmuir equation and assuming alternately that the vapor was C₁, C₂, and C₃. Only when the vapor was calculated as C₂ did the ΔH°_{298} remain essentially constant (202 ± 2 kcal/mole) and agree with the literature value (199 ± 5 kcal/mole). When calculated as C₃, the ΔH°_{298} is 220 kcal/mole compared with the literature value of 190 kcal/mole; this would indicate that if the evaporating species were C₃, the pressure is about 10^{-2} of the calculated equilibrium value. In similar manner, the data do not

Figure 9. Rate of vaporization of graphite as a function of temperature.

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not satisfy the values for C_1 . The rate of vaporization does agree with the predicted behavior if C_2 is the only species evaporating.

As the temperature is increased to 3400°K, a significant amount of the heat supplied goes into the vaporization process. The fraction radiated was determined from the temperature, surface area, and the total emissivity; the heat of vaporization was found by difference to be 100 ± 10 kcal/g-atom of carbon. The molar heats of vaporization at 3400°K of C_1 , C_2 , and C_3 are 170, 194, and 181 respectively; in terms of gram-atoms of carbon, they are 170, 97, and 60 kcal/mole, respectively. The evaporation of graphite as C_2 agrees with the observed heat of vaporization. While a combination of C_1 and C_3 could give this value, the earlier observation that the reaction of H_2 with graphite at 3400°K produces only C_2H_2 indicates that this is not the case.

It was found that, when the Pyrex vessel surrounding a graphite filament was heated at any temperature in the range 3000° to 3300°K and was immersed in liquid N_2 , the active species were trapped on the condensed surface which emitted light flashes when the liquid nitrogen was removed. The flashes came primarily from the surface but a significant number occurred in the vapor phase from particles of carbon which flaked off during the "sparkling." The light flashes were sufficiently intense to be readily photographed, and pictures taken at 1000 frames/sec indicated that their duration was < 1 msec. The color of the flashes appeared to vary from yellow at low intensities to white at high intensities indicating thermal emission; it was impossible to measure the emission spectra. Absorption spectra of the active cold deposit showed no definite absorption bands between 2000 and 6000 Å. There appeared to be some type of absorption below 3000 Å, but it may have been scattering. It is hypothesized that C_2 is adsorbed and stabilized on the glass-carbon surface at low temperature. Reaction of C_2 with small carbon aggregates on the surface, on warming, would release sufficient energy to heat the carbon locally to a high temperature, which would initiate recombination in adjacent C_2 molecules producing a chain reaction. The reaction $C_2 + C_n \rightarrow C_{n+2}$ should give off ≈ 100 kcal/mole.

Spectroscopic work on the composition of the vapor above graphite has continued. Photographic studies on the vapor inside thin-walled resistively heated graphite tubes in both helium and hydro-

gen atmospheres have revealed the C_2 spectrum in both absorption and emission. In addition, the CH spectrum was observed faintly in runs in hydrogen but no other C_xH species. No C_3 was observed photographically.

Further experiments were conducted by photoelectrically monitoring the intensity of the C_2 spectrum both in absorption and emission. The 0,0 bandhead at 5165.2 Å and the 1,1 bandhead at 5129.3 Å are the most intense bands observed for C_2 . The 5165.2 Å bandhead was used but there is some continuous radiation scattered from the walls of the graphite tube. The measured intensities of the C_2 radiation were corrected for this continuous radiation. This was done by making two identical runs, one at the C_2 bandhead and the other of the continuous background at a wavelength of 5 Å higher.

The data from 20 runs spanning the temperature range 2950° to 3275°K in atmospheres of Ar or He and pressures of 0.1 to 0.5 atm were used to obtain ΔH_0° values for C_2 by the second-law method. The values obtained were 189 ± 16 kcal/mole from emission and 192 ± 14 kcal/mole from absorption. This compares favorably with the values obtained from the mass spectrometer and optical spectrometer using King furnaces, where the "best" value is 195 ± 5 kcal/mole.

The absorption data were further utilized to obtain a value for the oscillator strength f_∞ of 0.0135 ± 0.004 at 3160°K. The literature values for this quantity show a wide range as follows:

Hagen	0.005 ± 0.003
Jeunehomme et al.	0.00433 ± 0.00012
Fairbain	0.032 ± 0.012
Sviridov et al.	0.022 ± 0.008
Harrington et al.	0.028 ± 0.009
Fink and Welge	0.016 ± 0.005
Barger and Broida	0.003

Our results fall near the middle of the range.

Photoelectric experiments also showed the presence of C_3 . This was not observed photographically but the high temperature continuum reported by Brewer et al. was followed on a point-by-point basis at 50-Å intervals from ≈ 4300 to 3100 Å. It had previously been followed to only 3700 Å by Engelke and by Marr. The integrated absorption gives an oscillator strength of 0.064 in good agreement with Barger and Broida's value of 0.06. The oscillator strength values all assume that C_3 is in equilibrium and that the $\Delta H^\circ_{3000} = 183$ kcal/mole C_3 .

Figure 10. Time dependence of apparent temperature readings on a graphite tube.

In carrying out runs in 0.5 atm He, the photoelectric pyrometer output dropped rapidly when the temperature reached 3200°K even though the power to the tube did not change. It was apparently caused by microscopic carbon particles which formed in the vapor from the recombination of evaporated species. The effect occurs not only with a broad-range 0.6 to 1.0- μ silicon photodetector, but also with a photoelectric pyrometer having a narrow band-pass (0.03 μ) centered at 0.653 μ , which is similar to a normal disappearing filament pyrometer. The effect would not be observed with the latter instrument, since it requires several seconds to take a reading.

The effect is dramatically shown in Figure 10, which is a graph of the apparent temperature as read on the photoelectric pyrometer vs the time, for several power levels. When a tube is heated at 4710 W in 0.5 atm of He, the temperature appears to rise to 3200°K, then drops off rapidly to 2800°K. At the termination of the heating pulse (3.0 sec), the trace rises to meet the anticipated temperature decay curve after a 0.1-sec lag. The absorbing species or particles were completely dispersed or condensed on the cell walls in ≈ 0.1 sec. Figure 10 also shows the same heating effect at 3690 W, while at 3130 W a normal heating curve is obtained.

When the tube is heated in 0.5 atm of H_2 , the effect is not observed, since, as the filament work has shown, the vaporized carbon reacts with the hydrogen forming hydrocarbons (C_2H_2 , C_2H_4 , etc.) which are transparent in the 0.6 to 1.0- μ range. This effect is also observed with 1-mm-wide filaments heated in He, but occurs at a higher temperature (3400°K) because the evaporating surface is much smaller. The nature of the interfering material was analyzed by measuring the extinction coefficient of light in the center of the tube from 3100 to 8250 Å. The results agreed with the values predicted for absorption and scattering by particulate rather than by molecular carbon.

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

Metal Hydrides

The reaction of hydrogen with a large number of alloys has been investigated. The main emphasis was on gas-solid equilibria and the determination of pressure-temperature-composition diagrams, but some kinetic data were obtained as well. The experimental techniques were essentially

Figure 11. Uptake of hydrogen by FeTi.

Table 4			
Partial Molar Thermodynamic Quantities in the System FeTi-H ₂			
Composition	$\Delta\bar{H}_{298}$, kcal/mole H ₂	$\Delta\bar{F}_{298}$, kcal/mole H ₂	$\Delta\bar{S}_{298}$, eu/mole H ₂
FeTiH _{0.1} } FeTiH _{1.0} }	-5.504	+0.891	-21.46
FeTiH _{1.3}	-6.996	+1.181	-27.44
FeTiH _{1.5}	-7.147	+1.247	-28.16
FeTiH _{1.7}	-7.633	+1.387	-30.27

the same as those previously described (BNL 50023, p. 36), but the ranges of temperature and pressure were widened in some cases. The chief practical goal has remained the achievement of hydrogen storage systems, but the properties of some of the hydrides investigated have suggested other applications; these are sketched out below.

IRON-TITANIUM ALLOYS

The system Fe-Ti forms two intermetallic compounds, Fe₂Ti and FeTi, which are stable below $\approx 1000^\circ\text{C}$. Fe₂Ti did not react with H₂ at a pressure of 400 psia between 25° and 400°C, nor did it react with H₂ between 25° and 100°C at a H₂ pressure of 900 psia. The compound FeTi reacted with H₂ rapidly at room temperature and a pressure of ≈ 900 psia. In Figure 11 are shown several pressure-composition isotherms for this system. It is apparent from the plateaus, ending in a steep rise in each curve at about the point corresponding to FeTiH, that there is a hydride phase of about that composition. The shape of the curves above that point suggests the existence of a higher hydride at about FeTiH_{1.8}, but they are also consistent with the continuous addition of hydrogen to a nonstoichiometric lower hydride. X-ray diffraction pictures will be required to distinguish between the possibilities.

In Figure 12 are shown semilog plots of the dissociation pressure vs the reciprocal of the absolute temperature, for several compositions. From these data thermodynamic functions were calculated, and these are shown in Table 4.

If Ti is present in substantial excess of the composition corresponding to FeTi, the pressure composition isotherm has a quite different shape (see Figure 13). A simplified interpretation of this

Figure 12. Dependence of dissociation pressure on temperature in the system FeTi-H₂.

Figure 13. Uptake of hydrogen by FeTi-Ti.

Figure 14. Uptake of hydrogen by vanadium.

curve can be given as follows: H_2 reacts with Ti to form stable titanium hydride until the $H/(Ti+Fe)$ ratio is ≈ 0.45 , at which point the FeTi phase reacts. The absence of any real plateau indicates that the system contains extensive solid solution regions.

VANADIUM AND VANADIUM ALLOYS

It is known that the vanadium-hydrogen system exhibits three different crystal phases at room temperature. From V to $VH_{0.05}$ is a solid solution of H in vanadium; $VH_{0.05}$ to $VH_{0.45}$ is a mixed phase region where a β hydride phase is introduced; and from $VH_{0.45}$ to $VH_{0.9}$ is pure β phase. Above $VH_{0.9}$ exists a third phase (γ) about which little, beyond the bare fact of its existence, has been published. Previously, the highest reported hydrogen content of vanadium hydride corresponded to a composition of $VH_{1.83}$. We have prepared vanadium hydride with a composition of $VH_{2.00}$ by exposing V to H_2 at $25^\circ C$ and 950 psia until a composition of $VH_{0.9}$ was reached, and then the entire system was cooled to $-75^\circ C$ while maintaining the H_2 pressure at 950 psia. In order to reach the maximum hydrogen content, it is

Figure 15. Dependence of dissociation pressure of VH_1 - VH_2 on temperature.

necessary to prepare and decompose the hydride several times. This procedure results in a porous metal substrate which is very reactive.

Figure 14 shows several pressure-composition isotherms of the vanadium-hydrogen system from $VH_{0.80}$ to $VH_{2.00}$. The plateaus show a slight downward gradient which may be caused by impurities in the metal (the V purity was 99.5%). The appearance of a plateau at $VH_{0.9}$ is noteworthy in that it tends to confirm previous work in which a tentative phase diagram for the vanadium-hydrogen was constructed from the results obtained in x-ray and neutron diffraction experiments. The reaction occurring in the plateau region may be written as

A semilog plot of the dissociation pressure vs the reciprocal temperature is shown in Figure 15. The curve is a straight line over the temperature range investigated and obeys the equation $\log P_{atm} = (-2064/T^\circ K) + 7.3405$. From these data, the following partial molar quantities have been calculated

Figure 16. Uptake of hydrogen by two vanadium alloys.

$$\Delta \bar{H}_{298} = -9.444 \text{ kcal/mole H}_2,$$

$$\Delta \bar{S}_{298} = -33.59 \text{ eu/mole H}_2, \text{ and}$$

$$\Delta \bar{F}_{298} = +0.565 \text{ kcal/mole H}_2.$$

The pressure-composition isotherms for two vanadium alloy-hydrogen systems are shown in Figure 16. Neither of these systems has been thoroughly investigated; however, they appear to resemble the V-H₂ system except that the upper portions of the isotherms are quite steeply inclined indicating that the compounds formed in that region are essentially nonstoichiometric.

Mg-Ni ALLOYS

The x-ray diffraction pattern of the compound Mg₂NiH₄ was indexed. The compound has a tetragonal crystal structure whose unit cell dimensions are $a = 6.464 \text{ \AA}$ and $c = 7.0333 \text{ \AA}$. The measured density of the compound was 2.57 g/cc which, when compared with the x-ray data, yields a value of 4 molecules per unit cell (the actual calculated number was 4.07).

Table 5

Hydrogen Uptake by Alloys

Alloy composition, wt %	Phase(s)	Absorbed wt %
60 Al, 40 V	VAl ₃	0.05
14 Al, 85 Zr	Zr ₂ Al	1.10
16 Al, 84 Zr	Zr ₅ Al ₃	1.32
55 Cr, 45 Al	Cr ₅ Al ₈	0.02
45 Al, 51 Ti	γ-Ti-Al + TiAl ₃	0.05
72 Al, 28 Ca	CaAl ₄	0.05
30 Al, 71 Nb	Al ₃ Nb + Nb	0.18
55 Al, 46 Co	Co ₂ Al ₅	0.05
70 Al, 31 Co	CoAl	0.05
55 Al, 45 Fe	Fe ₂ Al ₅	0.06
32 Al, 68 Ni	NiAl	<0.05
60 Al, 40 Ni	NiAl ₃	<0.05
15 Al, 85 Ni	Ni ₃ Al	<0.05
46 Al, 54 V	V ₅ Al ₈	0.05
69 Ag, 25 Ti	TiAg	1.00
59 Bi, 41 Ti	Ti ₁₃ Bi	0.9
7 B, 94.8 Co	Co ₂ B + Co	0.02
44 Ca, 54 Mg	Mg ₂ Ca	3.90
72 Ca, 28 Cu	Ca ₄ Cu	3.00
24 Ca, 76 Zn	CaZn ₂	0.91
42 Ca, 55 Mg	Mg ₂ Ca + Mg	3.88
41 Cr, 59 Mg	CrMg ₃	3.60
69 Cr, 30 Si	CrSi + Cr ₃ Si	0.03
49 Cr, 50 Ti	TiCr ₂ + Ti	1.20
40 Cr, 59 Ti	TiCr ₂	2.26
50 Cr, 50 V	Solid solution	0.05
73 Cd, 28 Mg	Mg ₅ Cd ₃	0.02
20 Cu, 80 Ti	Ti ₂ Cu + Ti	—
57 Cu, 43 Ti	TiCu	1.23
50 Co, 45 Ti	TiCo	1.35
27 Co, 73 V	V ₃ Co	0.10
67 Co, 33 V	VCo ₃ + σ _{V-Co}	0.04
59 Co, 42 V	σ _{V-Co}	0.10
49 Fe, 41 V	VFe	0.10
39 Mn, 61 Ti	TiMn + Mn	1.66
26 Mg, 73 Sn	Mg ₂ Sn + Sn	0.02
47 Mg, 53 Zn	Mg ₇ Zn ₃	3.00
27 Mg, 73 Zn	MgZn	1.03
23 Mg, 76 Sb	Mg ₃ Sb ₂	0.13
61 Nb, 38 Ni	NbNi	0.05
40 Nb, 60 V	Solid solution	1.87
35 Ni, 63 Ti	Ti ₂ Ni + Ti	2.39
77 Ni, 20 Ti	TiNi ₃	0.04
49 Ni, 49 Ti	TiNi + Ti ₂ Ni	1.50
61 Ni, 34 V	VNi ₂	0.01
53 Si, 45 Ti	TiSi ₂	0.02
43 Sn, 56 V	V ₃ Sn	0.32
30 Sb, 69 Ti	TiSb	1.40
50 Ti, 50 V	Solid solution	3.49
70 Ti, 30 V	Solid solution	3.84
25 Ti, 75 V	Solid Solution	3.24
10 Ti, 90 V	Solid solution	2.42

OTHER ALLOYS

Table 5 gives the results of an extensive screening program investigating the action of H_2 on metal alloys. The objective of these experiments was to find alloys that gave promise of reversibly absorbing large amounts of H_2 and that have high dissociation pressures at relatively low temperatures ($<300^\circ C$).

DECOMPOSITION KINETICS

The rate of evolution of H_2 from Mg_2NiH_4 was measured by allowing gas to expand from a container of the hydride into a region of much lower pressure. The rate appeared to be independent of the back pressure as long as it was not allowed to build up to over one fourth of the equilibrium pressure of the hydride. Figure 17 gives experimental results at three temperatures; they follow a first-order law. At $240^\circ C$ the rate constant was 0.014 sec^{-1} .

Figure 17. Rate of decomposition of Mg_2NiH_4 .

HYDRIDE APPLICATIONS

Some consideration has been given to uses for hydrides other than as hydrogen storage media. Preliminary analyses which were made on the following potential applications indicated that they are worth a more detailed study.

1) Heat-engine media. Hydrogen could serve as the working fluid in a heat engine, being "evaporated" from a metal hydride at the high temperature and "condensed" onto the depleted metal at the low. Certain advantages over the liquid-vapor Rankine cycle are envisaged, especially in small special-purpose engines.

2) Heat sources and sinks. Small portable generators of high or low temperature could be made from a two-hydride system. If a reservoir of a hydride which has a high decomposition pressure at room temperature is connected to a container of a metal capable of forming a more stable hydride, hydrogen will flow from the first to the second. The second will heat up, the first cool off, the rate of heating and cooling being precisely controllable by a valve. Later, the original state of the system can be restored by applying heat from an external source to the more stable hydride.

3) Hydrogen diffusers. There is reason to believe that thin layers of certain hydrides, deposited on a porous inert backing, may be very permeable to hydrogen and only to hydrogen. Such artificial membranes might serve as a replacement for the more expensive palladium-silver alloys now used to separate hydrogen from mixtures.

4) Temperature-regulating devices. Systems such as $VH_{0.8}$ - VH_2 - H_2 , which has a temperature coefficient of pressure of about 110 torr/ $^\circ C$ at room temperature, might find use as components of thermoregulators or fire alarms.

5) High-pressure sources. Systems like the last-named exert very high pressures on relatively gentle heating. Unlike explosives, they could be used repeatedly. J. REILLY, R. WISWALL, S. ARONSON

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Radiation Division

B. MANOWITZ

Radiation Research

D. METZ

SOLID-STATE REACTIONS

A study of the reactions between preirradiated crystalline amides and several gases has demonstrated that the processes are diffusion-controlled. The amides have a layer-like crystal lattice with the weakest intermolecular interactions occurring between the layers. The diffusion of gases through these structures can be described in terms of three components arranged in order of decreasing ease of diffusion as follows: (1) diffusion along crystal defects, such as dislocations, surfaces, etc., (2) diffusion between layer planes, and (3) diffusion orthogonal to the layers. These conclusions are arrived at by theoretical consideration and experimental data from a study of a series of amides of differing hydrocarbon chain length.

In those amides in which more than one radical can be trapped along the chain, it was shown that the radical farthest removed from the amide group reacts more readily than the other. This effect can be used to selectively react either radical with gases such as NO or O₂.

Further investigation of the previously reported reaction with SO₂ has shown that this molecule is too large to readily diffuse between the crystal layers, and that it reacts principally with radicals trapped along defects and surfaces. A quantitative comparison between those radicals accessible to SO₂ (at defects and surfaces) and those inaccessible (in the intact crystal lattice) indicates that the concentration of the former population is at least an order of magnitude higher than the latter.

G. ADLER, A. FAUCITANO, W. REAMS

RADIOLYSIS OF AROMATIC COMPOUNDS

The study of isomeric effects in the radiolysis of substituted aromatic compounds has been extended to include the nitrophenols and the fluoronitrobenzenes. Table 1 lists the results for the nitrophenols.

J. WEISS, N. CARCIELLO

MEMBRANE STUDIES

A program was started to investigate the properties of synthetic membranes. During the year the necessary equipment was built and tested on commercially produced cellophane. The effect of temperature, stirring speed, and direction were investigated. With specific ion electrodes, the transport of Na⁺, Cl⁻, Ca⁺², and NO₃⁻ was followed.

In addition to isothermal studies, several experiments were conducted with a thermal gradient across the membrane. The maximum temperature gradient that could be maintained was 43°C holding one side of the dialysis cell at $\approx 0^\circ\text{C}$.

Attempts were made to graft styrene to cellulose membranes and to fabricate membranes from vinyl chloride and acrylonitrile by using radiation polymerization techniques. This work is still under investigation.

Cellulose acetate membranes have been fabricated from solution by using standard techniques. Membranes from 1/2 to 2 mils thick have been produced, and testing of these membranes is in progress. J. WEISS, R. CHAPMAN, N. CARCIELLO

VINYL POLYMERIZATION MECHANISMS

A detailed comparison has been undertaken of the molecular weight distribution in exhaustively dried styrene, when the propagating species is pre-

Table 1

G-Values of Gaseous Products
in the Radiolysis of Nitrophenols
(At 120°C and 6.9×10^6 rad-hr⁻¹.)

	Ortho	Meta	Para
H ₂	0.007	0.007	0.006
N ₂	0.16	0.06	0.14
NO	0.012	0.	0.06
CO	0.039	0.016	0.011
CO ₂	0.13	0.052	0.071
Total gas	0.36	0.16	0.28

dominantly an ion or ions, with that obtained in normally dried styrene, which propagates by a free radical mechanism. The samples, for both degrees of dryness, have been prepared over wide temperature and dose rate ranges. The distribution curves are now being analyzed for kinetic significance.

The temperature dependence of the polymerization rate of very dry α -methylstyrene, over a wide dose rate range, is currently under investigation. Linear dependence of the logarithm of the rate versus reciprocal absolute temperature has been observed between $+20^\circ$ and $+80^\circ\text{C}$ at dose rates ranging from 1×10^3 to 1×10^6 rad-hr. The Arrhenius temperature coefficient in this range of the parameter is ≈ -9 kcal-mole $^{-1}$. Between $+20^\circ$ and -20°C there appears to be an almost zero temperature coefficient.

Since α -methylstyrene normally exhibits a "ceiling" temperature of $\approx 61^\circ\text{C}$ (a temperature above which no net conversion to polymer occurs because of an equilibrium between the propagation and depropagation reaction), the Arrhenius behavior of this monomer under the present experimental condition is novel and is under further investigation. D. METZ, A. GLINES, C. JOHNSON

THE RADIOLYSIS OF NITROUS OXIDE

The yields of nitrogen and oxygen were measured for the irradiation of nitrous oxide in the solid, liquid, and gaseous (up to 0.7 g/cc $^{-1}$) states, with Co^{60} γ rays as well as α particles from Po^{210} and Rn^{222} . The results are shown in Table 2. There is a remarkable constancy in the value of $G(\text{N}_2)$. Addition of electron scavengers (SF_6 , NO_2 , or CCl_4) decreases $G(\text{N}_2)$ by a maximum of 25%. These results and information already available suggest that energy-dependent electron reactions are important in the radiolysis of nitrous oxide.

J. SEARS, J. SUCHER

RADIOLYSIS OF LIQUID AMMONIA

Because of uncertainties about the purity of the distilled water supply, certain experiments in this series were repeated. Above 1×10^5 rads the presence of an azide was reconfirmed. Below this dose, the results are irreproducible, and it is not possible to definitely ascribe previously observed spectra to species formed in the radiolysis or to impurities. No dose rate effect, between 3×10^4 and 1×10^6 rad/hr and at a total dose of 1×10^5 rads, has been

Table 2
Nitrogen Yields in the Radiolysis of Nitrous Oxide

Physical state	Pressure or density	Irradiation source	Temperature, $^\circ\text{C}$	Additive	O_2/N_2	$G(\text{N}_2)$
Gas	440 to 680 torr	Po^{210} (α)	25	—	0.20 ± 0.01	10.0 ± 0.4
Gas	574 torr	Rn^{222} (α)	25	—	0.11	7.6
Gas	660 to 1000 torr	Co^{60} (γ)	10	—	0.18 ± 0.02	9.9 ± 0.5
Dense gas	0.02 g/cc	"	38	—	0.16	11.2 ± 0.9
"	0.035 g/cc	"	"	—	0.135	11.2 ± 0.8
"	0.10 g/cc	"	"	—	0.15	10.6 ± 0.9
"	0.30 g/cc	"	"	—	0.13	12.1
"	0.40 g/cc	"	"	—	0.12	12.3
"	0.55 g/cc	"	"	—	0.12	13.5 ± 0.6
"	0.70 g/cc	"	"	—	0.15	11.6 ± 0.5
Liquid	1.19 g/cc	"	-78	—	0.20 ± 0.01	11.2 ± 0.5
Solid	1.5 g/cc	"	-196	—	0.19 ± 0.01	10.6 ± 0.6
Gas	800 torr	"	10	CO_2 , 8 to 60 torr	0.23 ± 0.03	9.4 ± 0.6
"	"	"	"	SF_6 , 0.1 to 8 torr	0.28 ± 0.04	7.25 ± 0.6
"	"	"	"	NO_2 , 0.45 to 15 torr	—	6.8 ± 0.4
"	"	"	"	CCl_4 , 1 torr	0.16	7.7 ± 0.5
"	"	"	"	CCl_4 , 3 torr	0.12	6.7 ± 0.7
"	"	"	"	CCl_4 , 8 torr	0.11	6.7 ± 0.4
"	"	"	"	CCl_4 , 14 torr	0.04	6.8
Dense gas	0.70 g/cc	"	38	SF_6 , 0.5%	—	8.4 ± 0.3

observed for hydrazine formation. Preliminary studies, in which liquid ammonia is saturated with hydrogen gas (1 atm), show no change in hydrazine yield. J. SUTHERLAND, R. GOODRICH

RADIOLYSIS IN THE ABSORBED STATE

The radiolysis of nitrous oxide on Linde 13X has continued. It has been found that pretreatment of the sieves with oxygen prior to irradiation improved the material balance in the reaction, i.e., the $G(\text{O}_2)$ values increased while $G(\text{N}_2)$ values were unaffected. The effect of temperature has been studied. Linde 13X sieve develops a pink color on irradiation at dry ice and at liquid nitrogen temperatures. This color disappears on warming to room temperature. When N_2O is adsorbed no color is observed, but nitrogen is released at temperatures $> -78^\circ\text{C}$ even in those samples irradiated at liquid temperature. This effect is being studied in greater detail. J. SUTHERLAND

Figure 2. Homogeneous irradiation of air.

Chemonuclear Program

M. STEINBERG

FISSION FRAGMENT AND RADIATION CHEMISTRY

Nitrogen Fixation

Homogeneous Gas-Phase Experiments. The series of capsule experiments irradiating $\text{N}_2\text{-O}_2$ mixtures at ≈ 5 and ≈ 68 atm at 20° to 50°C with

Figure 1. Flow system for chemical synthesis by radiation.

Co^{60} γ , pile radiation, and fission fragment radiation sources was completed. The higher temperature runs (up to 550°C) will be reserved for in-pile experiments in a flowing system with the chemonuclear loop.

A once-through flow system for preliminary studies of the homogeneous fixation of $\text{N}_2\text{-O}_2$ was set up in a Co^{60} γ field. A schematic of a typical stainless steel flow system for chemical production by Co^{60} γ irradiation is shown in Figure 1, and several results for the formation of NO_2 are shown in Figure 2. The G -value for NO_2 formation has a maximum between 500° and 600°C , increases slightly with increasing flow rate, and decreases with increasing pressure in the temperature range of interest. By least-mean-square analysis it was shown that the intensity and reciprocal space velocity dependence of the NO_2 effluent concentration is

$$C_{\text{NO}_2} \propto I^{0.95 \pm 0.02} (1/SV)^{0.90 \pm 0.02}$$

And in a more detailed multiple linear regression it was further shown that

$$C_{\text{NO}_2} \propto (1/SV)^{0.92 \pm 0.02} (\text{N}_2)^{1.03 \pm 0.02}$$

with the NO_2 concentration being completely independent of the O_2 concentration in the range 3 to 78% N_2 . Since the rate of the reaction has been found to be

$$dc/d(1/SV) \propto I^{0.95}(N_2)^{1.03},$$

the rate-determining step is most assuredly the formation of one or more active N_2 species by direct irradiation. The variables ranged from 0.5 to 5.2 Mrad/hr, 100° to 650°C, 15 and 69 atm, and 0.3 to 3.0 min ($1/SV$). The effects of increased surface-to-volume ratio and a glass-lined stainless steel vessel were negligible. Some experiments will be performed at 200 atm and <15 atm to clarify the pressure dependency, and static experiments will be conducted to determine the equilibrium concentration. The data plotted in Figure 2 indicate a maximum $G(NO_2)$ value of 3.4.

Heterogeneous Experiments – Bubbling Experiments. Further investigation was made on the yield of NO_3^- , NO_2^- , and NH_3 in the liquid phase when irradiating air bubbling through water in a Co^{60} γ field. The data indicate that $G_t(N)$ - and $G_g(N)$ -values for fixation of nitrogen based first on the total gas in the bubbles and dissolved in the liquid and second on the gas in the bubbles only are much above the value of 1 to 2 obtained by homogeneous gas irradiation for nitrogen fixation. The concentration and G -values appear to be an increasing function of the pressure reaching $G_g(N)$ -values as high as ≈ 58 at ≈ 100 atm. However, most of the γ energy is absorbed in the liquid water phase. Attempts at reversing the phases by spraying liquid water into N_2 - O_2 gas yield $G(N)$ -values no higher than ≈ 6 . Further experiments are being carried out to clarify the anomalously high G -values in the gas phase when bubbled through water. Caustic solutions yield only oxides of nitrogen with no reduced nitrogen as ammonia.

Ozone Synthesis

An appreciable effect from cooling the reaction vessel for ozone formation has been noted. For example, for 97% O_2 under a pressure of 69 atm, a dose rate of 0.62 Mrad/hr, and a flow of 110 cc/min through a 30-cc vessel at room temperature, a steady-state O_3 concentration of 6 ppm at a G -value of 1.1 was obtained; at $-100^\circ C$, 216 ppm at a G -value of 14.1. An important accomplishment was the development of a cooling system capable of controlling $-100^\circ C$ temperatures to within $1^\circ C$ for a flow reaction vessel in a 2½-in. radiation tube. The flow diagram is similar to that shown in Figure 1. It was also found that a small amount of N_2 (3%) caused about a 3-fold increase in the rate of formation of O_3 , as compared with

that from pure O_2 . This effect is currently being investigated and, in view of the favorable yields and rates at low temperatures, the effects of temperature, pressure, gaseous additives, intensity, surface-to-volume ratio, and wall material will be studied prior to the addition of solid materials. The flow system will most probably be investigated with O_2 in the liquid state also.

An encouraging observation is that the G -value increases as the square root of the pressure.

The possible wide-scale application of ozone in water pollution control and treatment has led to investigations of improvements in high-voltage discharge synthesis, such as radio frequency plasmas and synergistic effects with radiation. The work is directed mainly toward exciting the vibrational states of oxygen.

The fact that a $G(O_3)$ value of ≈ 15 is attainable indicates that chemonuclear reactors for ozone synthesis for the large scale treatment of water may be economical.

R. DIETZ,
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CHEMONUCLEAR IN-PILE RESEARCH LOOP

Construction of the Chemonuclear In-Pile Research Loop (CIRL) was completed during the latter part of 1968. Some of the shielding panels remain to be put in place, but they will not be positioned until just before the beginning of fueled operations.

In November the first loop run was made (see Figure 3) with the BGRR critical; its purpose was to determine the flux and dose-rate distributions along the in-pile section. The reactor was run up to 15 MW and operated for a 10-hr period without incident. Capsules containing N_2O for total dose [γ plus (n, p) reaction on nitrogen] and CO_2 with NO_2 for γ dose alone were inserted at six points along the in-pile section, and a cobalt wire was run inside the section for thermal neutron flux determination. These were mounted together as a single unit for insertion and removal. Analyses were run on the capsule contents, and the cobalt wire was cut up into 1-in. segments and counted. In order to eliminate thermal effects, nitrogen gas under 100 psig pressure was circulated through the loop during the run to keep the temperature of the capsules at $100^\circ F$.

During the past year, considerable time was spent in completing the instrument and power systems for the loop and in debugging and calibrat-

ing them. This was particularly time-consuming, since earlier in the year the Engineering Division's instrumentation group, which was handling the job, was disbanded and it became necessary for Radiation Division personnel to take over the partially completed system and finish it.

Prior to the first reactor run, the out-of-pile portion of the loop was operated independently of the in-pile section, using a shunt to bypass the in-pile section. The series of runs made covered the full operating range of the loop, with respect to temperature, pressure, and flow rate. This provided the opportunity to gain operating experience with the loop, determine the loop's characteristics, cali-

brate instruments, and provide a shakedown period to establish and correct malfunctions. The temperature specifications (the ability to supply gas from -30°F to 800°F to the in-pile section and to keep it below 200°F after the cooler) was met and the loop was operated at pressures from 100 to 1000 psig. Faulty valves, gages, and one flowmeter were located and repaired or replaced. The entire loop was leak-checked. The suitability of the loop for operation with 1000 psig oxygen was reviewed, and some modifications made in the vacuum system. The section was then checked out with oxygen under pressure.

Considerable effort went into making the gas-bearing compressors, designed to circulate the gas in the loop, operational. The machine purchased from Société Rateau was the one initially installed. The high 60-Hz starting current required by this machine was beyond the capability of the variable-frequency motor-generator, so it was necessary to start it directly across the main line. After a few short runs, it was not possible to start it at all. It was taken out of the loop and disassembled. Considerable wear was found on the impeller-end alumina bearing surfaces. After replacing the pads with a new set supplied by Rateau, the same difficulty in starting and the same wear-pattern were observed. Mechanical Technology, Inc. was consulted, and it was agreed to replace the alumina on the impeller-end bearing surface with chrome oxide (which has better wear characteristics), rebalance the rotor and impeller, and readjust the bearing clearances. Since these steps were taken, the machine has been started several times across the line and has been run without difficulty. It has been reassembled and is now in readiness as a spare. In the meantime the stator canning, testing, and reassembly of the MTI compressor was completed by BNL. The machine was installed in the loop in place of the Rateau and has operated without incident. To date it has made 35 starts and stops and has run a total of 95 hr at speeds from 3000 to 15,000 rpm. It has been operated at pressures from atmospheric to 1000 psig and at temperatures from -30° to 200°F , running on oxygen, nitrogen, and mixtures of the two. The flow rates attainable appear to be about 15% less under some conditions than the manufacturer found during testing at his plant. This is being resolved.

A safety review of the CIRL was written and submitted to the Reactor Critical Experiments

Figure 3. At the control panel of the Chemonuclear In-Pile Research Loop on the occasion of the first operation are, from left to right, M. Steinberg, W. Tucker, E. Cote, S. Sato, M. Beller, and J Klein.

and Safety Committee for their consideration. After a series of meetings with the Committee, a revised document was prepared and operation of the loop approved by the Director's Office. AEC approval for operation of the loop has also been obtained.

Beginning in January 1969, it is planned to operate the CIRC about every fourth week, when the operating schedule of the HFBR permits operation of the BGRR. Runs will cover flow dosimetry, production of ozone from oxygen, NO₂ from nitrogen-oxygen mixtures, and carbon monoxide from carbon dioxide. The initial runs will be made without fuel, using reactor gammas and neutrons to establish a background. Fueled runs will then follow. Prior to loading fuel into the loop, each of the three sizes of honeycomb fuel will be checked for ability to withstand the temperature and flow conditions to be met in the in-pile section.

W. TUCKER, M. BELLER, J. KLEIN, G. ARNOLD,
E. COTE, J. HARE, S. SATO

Radiation Chemical Processing

M. STEINBERG

ETHYLENE HOMOPOLYMERIZATION

The general objective of this program is to develop radiation chemical processes for the polymerization of ethylene. Secondary objectives include the development of the fundamentals and principles of high-pressure radiation-induced processes utilizing isotopic radiation sources with the emphasis on Co⁶⁰.

As a result of the BNL program, a number of industrial firms have undertaken continued process development of the radiation-induced polymerization of ethylene on a pilot plant scale. Because of this specific industrial research effort, based on or stimulated by the BNL program, the experimental effort on the radiation-induced polymerization of ethylene was curtailed at BNL. The flow system (Figure 4), consisting of compression equipment, a 100-cc reaction vessel in the water tank type Co⁶⁰ γ facility, and all thermal and pressure control apparatus, is now being maintained in standby operating condition (Figures 5 and 6).

The current BNL effort in this area consists mainly of meeting with industrial organizations having an interest in radiation chemical proc-

essing and specifically in the polymerization of ethylene. Each organization, whether new in the polyethylene processing field or currently marketing polyethylene, is given a briefing on the BNL process. Any requests for samples of radiation-produced polyethylene are filled.

In addition to meeting with industrial representatives, an international information exchange agreement has been arranged with the Japanese Atomic Energy Research Institute laboratory at Takasaki. The Takasaki Laboratory is a relatively large radiation process development laboratory and has adopted as one of its projects the development of a radiation process for production of polyethylene under conditions below its melting point ($\approx 120^\circ\text{C}$). This system is based on the chemistry, kinetics, and process designs developed earlier at BNL. Pilot plant work has been done at Takasaki on this low temperature system and is a good supplement to the pilot flow experiment at BNL on the high temperature (above the melting point) system. The low temperature system produces intermediate density (0.93 to 0.94 g/cc) high molecular weight polyethylene, a product which is relatively new on the market, whereas the high temperature process yields low density (0.91 g/cc) film grade polyethylene which enjoys a very large market. To date reports have been exchanged between the two laboratories, and a meeting at BNL between personnel of the two laboratories was held in November 1968.

In the area of the copolymerization of ethylene, there has been much industrial interest in the research performed at BNL in the past on the copolymerization with 20 different monomers. Primary interest has been in the ethylene-carbon monoxide (Et-CO) and the ethylene-sulfur dioxide (Et-SO₂) systems. Information exchange meetings are periodically being held with industrial representatives at BNL. Requests for samples have exceeded the supply.

It is planned to continue maintaining the ethylene polymerization equipment and to hold information meetings with interested U.S. industrial organizations and with the Japanese-Takasaki Laboratory. It is also planned to perform additional experiments in the Et-CO system both from the point of view of obtaining additional sample material for characterization and for the design of pilot plant equipment. Construction of equipment for the batch production of the polyketones is being considered.

Figure 4. Diagram of flow system for the radiation polymerization of ethylene.

Figure 5. Flow system for the radiation polymerization of ethylene showing the stainless steel jacketed reaction vessel assembly (right) and the product discharge line installed in the irradiation facility. Surrounding the reaction vessel is the radiation source holder containing 5000 Ci Co^{60} in the form of six BNL standard sources. Radiation shielding is provided by ≈ 12 ft of water. Ethylene gas is introduced into the top of the vessel. The molten polyethylene flows through the heated discharge line to the product separator located adjacent to the irradiator.

Figure 6. The radiation polymerization of ethylene showing the pneumatically operated control valve through which the polymer is discharged. The valve is located at the top of the product discharge line shown in Figure 5. The mixture of polyethylene and unreacted ethylene from the reaction vessel is expanded across the valve. The polymer is collected and the ethylene vented.

COMPOSITE MATERIALS

Concrete-Polymer Materials

The preparation, testing, and development of concrete-polymer composites as improved materials of construction are under investigation in a joint program being carried out with the U.S. Bureau of Reclamation. The studies include the development of methods of preparation of both preformed and premixed concrete-polymer composites. The preparation techniques for preformed concrete consist of drying, evacuation, monomer soaking, coating, and *in situ* polymerizing the monomer either by Co^{60} γ radiation, by thermal-catalytic initiation, or by a combination of both. For the premix concrete either part of the water is replaced with monomer or monomer is added to the fresh concrete mix. The mix is subsequently radiation or thermally polymerized. Some of the samples that have been prepared are shown in Figure 7.

It has been shown that preformed air-entrained concrete and mortar can be fully impregnated with a monomer polymerized *in situ* either by radiation or thermal-catalytic techniques. Monomers

Figure 7. Samples of concrete-polymer composites.

tested in survey experiments included ethylene, ethylene- SO_2 , vinyl acetate, acrylonitrile, methyl methacrylate, styrene, styrene-acrylonitrile, 10% trimethylolpropane trimethylacrylate-methyl methacrylate, polyester-styrene, and epoxy-styrene. The ethylene gas produced a fine white powder dispersed through the void volume of the concrete. The liquid monomers gave a continuous hard deposit through the concrete.

The highest degree of polymer loading obtained with air-entrained concrete containing type II cement is 6.7% by weight of the dried unimpregnated concrete or $\approx 14\%$ by volume. This comes close to completely filling the available void volume in this type of concrete.

An extensive series of tests have been carried out with polymethyl methacrylate impregnated concrete and polystyrene impregnated concrete. The improvement in structural properties has been found to be an increasing function of the weight loading of the concrete. The degree of weight loading depends on the dryness of the concrete.

One procedure to obtain maximum polymer loading with methyl methacrylate is to oven dry the concrete specimen to constant weight at temperatures of 105°C or higher, evacuate the air to $< \approx 3$ in. Hg, absolute pressure, soak in liquid monomer, wrap in polyethylene film, and irradiate at ambient temperature to a dose of 1.5 Mrad at a dose rate of 2.5×10^5 rads/hr. Polymerization can also be obtained by heating the impregnated concrete to 77°C for 2 hr with 2% benzoyl peroxide catalyst added to the monomer. Cylindrical specimens up to 6 in. diam $\times$ 12 in. long have been fully impregnated. A summary of the properties for maximum loading with methyl methacrylate is given in Table 3.

Remarkable improvements in properties compared with control specimens of untreated concrete have been obtained as follows:

(a) Compressive strength increases of 285% over control or a factor of almost four times the compressive strength of the control.

(b) Tensile strength increases of 290%.

(c) Modulus of elasticity increases of 80%.

(d) Modulus of rupture increases of 256%.

(e) Flexural modulus of elasticity increases of 44%.

(f) Resistance to freeze-thaw is improved by $> 300\%$.

(g) Water permeability decreases to negligible values.

Table 3
Summary of Properties of Concrete-Polymer Material

	Concrete control specimen (type II cement)	Concrete with up to 6.7 wt % loading; polymethyl methacrylate; Co ⁶⁰ γ radiation polymerized
Compressive strength, psi	5,267	20,255
Tensile strength, psi	416	1,627
Modulus of elasticity, psi	3.5×10^6	6.3×10^6
Modulus of rupture, psi	739	2,637
Flexural modulus of elasticity, psi	4.3×10^6	6.3×10^6
Coefficient of expansion, in./in./°F	4.02×10^{-6}	5.36×10^{-6}
Thermal conductivity at 23°C, Btu/hr/ft/°F	1.332	1.306
Water permeability, ft/yr	6.2×10^{-4}	0
Water absorption, %	5.3	0.29
Freeze-thaw resistance		
Number of cycles	590	2,420
% wt loss	26.5	0.5
Corrosion to sulfates (300-day exposure, % expansion)	0.144	0
Corrosion to distilled water	severe attack	no attack

(h) Water absorption decreases by as much as 95%.

(i) Corrosion resistance to distilled water and sulfate brines has been improved 100%.

The coefficients of expansion, specific heat, and diffusivity have been measured. The resistance to abrasion, cavitation, soluble sulfates, and acid corrosion have shown significant improvements.

Methyl methacrylate impregnated concrete-polymer specimens subjected to creep tests exhibited an expansion under sustained load (negative creep). This is opposite to the normal contraction in length (positive creep) of ordinary concrete. Further investigation of this highly unusual phenomenon of negative creep is necessary, since this property could have a significant influence on the design of concrete-polymer structural and pre-fabricated members.

It was found that thermal-catalytically polymerized concrete-polymer gave from 7 to 15% lower strength values than Co⁶⁰ γ radiation polymerized. Polystyrene impregnated concrete gave $\approx$ 30% lower strength values than polymethyl methacrylate. It was also noted that cracking of the concrete occurred in undried specimens when impregnated with styrene and polymerized by radiation. There was no cracking with styrene impregnation of dried and irradiated concrete or with styrene impregnation of dried and undried thermally treated concrete.

Radiation and thermal treatment of unimpregnated concrete gave no improvement in structural properties. The improvement in properties is thus attributed to polymer impregnation.

A series of test specimens with crosslinked polymethyl methacrylate have been prepared and await the results of tests.

In the case of premixed concrete-polymer preparations, improvements in compressive strength and water absorption were obtained with styrene and acrylonitrile additions. The maximum improvement (87% in compression with acrylonitrile) was much lower than that with impregnated preformed concrete. In the case of methyl methacrylate premixed, there was a marked decrease in compressive strength. Substitution of methyl alcohol for water inhibited the hardening of concrete.

High strength OSW concrete (type V cement, air-entrained with fly ash and aggregate) impregnated with methyl methacrylate gave the highest value of compressive strength, 22,630 psi, equivalent to a 164% improvement over untreated OSW concrete.

The fine structure of the concrete-polymer material is being examined by optical and electron microscopy and petrographic techniques. Fundamental studies are in progress to obtain an understanding of the bonding of the polymer to the concrete on a micro scale. These studies show that, for preformed concrete at higher loadings, the im-

pregnation was fairly complete and that the polymer coats most of the internal surfaces of the void passages in the concrete. In the premix concrete the polymer distribution varied from poor to good.

A generalized cost comparison with other common construction materials, using as an index the ratio of the unit material cost of the finished product to its strength, indicates that concrete-polymer

(polymethyl methacrylate) in compression is far superior to concrete alone, to plastic alone as well as to steel and aluminum. However, in tension the concrete-polymer is second best to steel and aluminum but better than either concrete or plastic alone.

In terms of durability, i.e., resistance to freeze-thaw (Figure 8), water absorption, corrosion re-

Figure 8. Control concrete (not impregnated) (left), after 590 cycles in freeze-thaw test. Cylinder shows a 26.5% weight loss. Concrete impregnated with methyl methacrylate and polymerized by radiation (right), after 2420 cycles in the severe test. Cylinder shows a 0.5% weight loss.

sistance, etc., concrete-polymer offers a large improvement over concrete alone. The combination of significant improvement in properties obtained with relatively low concentrations of low cost monomers gives the material a definite economic potential.

Several possible applications of concrete-polymer have been investigated in a preliminary manner. These include concrete-polymer sewer and pressure pipe, building materials in housing, underwater structures, corrosion resistant concrete for desalination plants, and antifracture concrete. The composite appears to have low maintenance qualities and high aesthetic value.

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J. VARELA, K. KANIGE

HETEROGENEOUS RADIATION CHEMISTRY

The main objectives of these studies are to investigate the effects and application of radiation and catalysts on chemical reactions both from the point of view of improving existing catalytic reactions and improvement of homogeneous reactions. Radiation treatment is performed primarily during the reaction in the presence of solid catalysts but also the effect of preirradiation of the catalyst substrate is examined.

From the initial experiments in radiation chemistry to the present status, considerable interest has arisen as to the possibility of energy transfer from solid material in a radiation field to gases absorbed on or in contact with the solid. Energy transfer was reasoned to have occurred when the G_0 -value (the radiation yield in molecules per 100 eV of energy absorbed in the gas phase only) exceeded the maximum value for an endothermic reaction based on thermochemical considerations.

The decomposition of CO_2 was studied in detail in both capsule and flow systems with the main conclusions being that absorbed H on solid catalysts is responsible for the high initial yields in capsule experiments and that the highest G -values in the flow system were obtained with solids which did not strongly adsorb either CO or O_2 . Energy transfer was shown to occur in the capsule experiments but the results were not conclusive in the flow system. The study of this reaction has been completed.

Two other reactions suitable for energy transfer studies and also of potential practical application are the fixation of N_2 and the formation of O_3 ,

both currently being studied. The purpose of the present work is (1) to attempt to determine a satisfactory mechanism for the homogeneous irradiation formation and (2) to explore the use of solid additives for possible energy transfer effects. The results of the homogeneous investigation should aid in the selection of solid materials and also provide information for the initial experimental approach in the Brookhaven chemonuclear program on application of nuclear reactor radiation. These results are reviewed under chemonuclear radiation and fission fragment chemistry.

The synthesis of ozone from oxygen in the liquid phase with solid catalyst materials is being investigated, varying the surface-to-volume ratio.

The irradiation decomposition of iron pentacarbonyl adsorbed on molecular sieve is being investigated for the purpose of making an improved iron catalyst for the synthesis of ammonia. The thermal decomposition did not produce any activity and evaluation of the effects of irradiation have yet to be made. Other interesting experiments for studying energy transfer are the steam methanation of coal, the decomposition of steam over high surface area adsorbents such as silica gel, and others. Practical chemical application of Co^{60} can be attained in some of these systems if either energy transfer can be made to occur efficiently or more optimized homogeneous conditions are reached.

M. STEINBERG, R. DIETZ

RADIATION EFFECTS ON ELECTRODE REACTIONS

A program to investigate the use of radiation as a means of promoting electrode reactions is in progress. This program seeks to obtain more powerful oxygen electrodes, i.e., electrodes capable of delivering higher currents at higher voltages, by treatment of the electrodes and electrolytic cell with Co^{60} γ and Sr^{90} β radiation. The study is directed toward improving the highly irreversible air (and oxygen) electrode for both industrial electrolysis and fuel cell power production purposes.

Oxygen Electrode Studies

Work was initiated with platinum, the best catalyst known whose corrosion resistance is outstanding in the electrolytes chosen for study. The behavior of the oxygen electrode on platinum in 1 M H_2SO_4 was studied experimentally under the influence of Co^{60} γ radiation at the HIRDL. Substantial gamma effects have been observed and

Figure 9. Current density vs potential at platinum in sulfuric acid.

from the observed increases in limiting currents with radiation dose, a G -value as high as 2.5 was estimated for the production of hydrogen peroxide. The influence of dose rate on the G -value was also determined. An inverse relationship was found and the G -value had declined to 1 at the highest dose rates. The result that the γ irradiation of aqueous electrolytes increases one limiting current carried at an inert electrode under controlled potential conditions is in keeping with the known generation of radiolysis products. Ways are now under consideration to increase the current yield beyond the values reported here.

The current-voltage enhancement summarized above was obtained in an apparatus specially designed to be inserted in the HIRDL water-cooled experimental tubes. Radiation-resistant container materials were used, and a shielded platinized platinum hydrogen reference electrode was incorporated to avoid contamination from the reference electrode. Linear potential scans were made, the current being recorded prior to, during, and after irradiation of the cell. The dose rate was

Figure 10. Influence of dose rate on limiting current density.

varied by simply transferring the entire experimental assembly into tubes of progressively higher dose rates. The current versus voltage behavior of the irradiated and unirradiated electrodes is shown in Figure 9. It will be seen that currents are larger in the anodic region as well as the cathodic region. At potentials between 1.1 and 1.4 V, a limiting current density is observed in the anodic region. This limiting current density was found to depend on the time and the dose rate as shown in Figure 10. Upon making the assumption that the limiting current density is associated exclusively with the production and subsequent oxidation of hydrogen peroxide, the G -value for the radiolysis was estimated.

Corrosion Studies of Materials for Oxygen Electrodes

In an effort to substitute low cost materials for platinum as substrates for the oxygen electrode reaction, corrosion studies were conducted by applying controlled potential to simulate the conditions of oxygen electrodes in service both in acids

and bases. In acid media, glassy carbon, Au, Nb, and Zr are possible substitutes for platinum. Similar testing in basic media suggest a much wider field of low cost materials having acceptably low corrosion rates. The response of these materials to irradiation treatments is unknown.

Reference Electrodes

The sensitivity of the saturated calomel electrode (SCE) to doses of γ radiation equal to 1×10^6 rad of Co^{60} was found to produce <2 -mV potential shift compared with a group of unirradiated electrodes. The potential difference vanished in time and is thought to be traceable to thermal phenomena rather than to radiolysis effects. Similarly an assembly consisting of an SCE vs a Ag/AgCl reference electrode both in saturated KCl will expand for 10 min at a dose rate of 11.7×10^6 rad/hr. The initial potential difference of 44.5 mV increased to 48 mV during the irradiation but returned to the initial condition a short time after irradiation.

During the next period the influence of pH will be examined by the use of strong NaOH electrolyte. The previously mentioned corrosion results provide a basis for the selection of promising low cost electrode materials to be tried as electrodes in the radiation environment. Since hydrocarbon oxidation reactions are also known to be kinetically slow, the possible advantages to the use of radiation in this area will be examined.

Types of radiation other than Co^{60} γ such as neutron, α , or β radiations are of considerable interest for their possible effects on electrode substrates as well as electrolytes.

J. McNICHOLAS, W. HORN

SURVEY EXPERIMENTS ON APPLICATION OF ISOTOPIC RADIATION FOR CHEMICAL PROCESSING

In the search for applications of isotopic radiation energy for chemical processing, exploratory experiments are performed to determine the existence of a radiation-induced chemical effect and subsequently once this is established a determination of the radiation chemical yield is made. The criteria for selection of systems are based on both novelty or economically promising processes. The following reviews some of the topics touched upon during the current year.

Polymer Composites

The application of Co^{60} γ radiation induced *in situ* polymerization of monomers in wood for formation of wood-plastic composites and of the recent development at BNL of concrete-polymer composites has led to the investigation of other possible polymer composites of potential commercial interest as follows.

Experimental work has been initiated on aggregate-polymer composites eliminating cement additions. The aggregate could be rock formations, such as granite, foamed glass, sand, or soil. The proportion of aggregate in these composites would be high relative to monomer addition. The objectives of these experiments are to determine whether potentially useful low cost materials can be formed, to measure their properties, and hopefully, to elucidate the mechanism of property improvement for these highly filled composites. A number of government agencies including the Army, Navy, Bureau of Standards, and Department of Agriculture have shown interest in investigating these types of composites.

Desulfurization of Oil

The original conception for this exploratory investigation was to partially oxidize the sulfur groups in the refractory organic ring compounds, e.g., thiophene, in oil and coal with oxygen or air in the presence of a radiation field at ambient temperatures. In this manner, the existing water insoluble sulfide compounds would be converted to water soluble sulfonic acid compounds and would be easily removed by a water wash. The basis for this, as evidenced in the literature, is that thiophene can be converted to the sulfonic acid derivative in the presence of oxygen and a Co^{60} γ radiation field in relatively high chain yields. With this in view, a number of experiments were performed bubbling air through a 50:50 volume mixture of No. 6 fuel oil and water in a Co^{60} γ radiation field. The oil contained 2.2% sulfur. Co^{60} doses up to 100 Mrad at dose rates of 1 Mrad/hr and at pressures up to 140 atm under flowing conditions were used. As reported earlier, air analysis of the oil mixture at the end of the run indicated sulfur reductions of from 36 to 50% of the initial sulfur concentration. However, it was noted that there was a deficiency of the water recovered at the end of each run. Furthermore, the sulfur analysis of the aqueous layer indicated an insufficient

quantity of sulfur as sulfate compared with that which would be expected by the solubilization of the organic sulfur removed from the fuel oil. An examination of the oil layer indicated the presence of a significant quantity of water. In effect, an emulsion of water and oil was formed because of the air agitated conditions, and it appeared to be extremely stable. The sulfur reduction was, therefore, being obtained as a result of water dilution and not by water solubilization. It is planned to run several additional experiments with air flowing but without water, and then the irradiated oil will be washed with water or dilute caustic to avoid this emulsifying effect. These final tests should determine the efficacy of the radiation-induced partial oxidation of aromatic sulfur containing compounds that are present in fuel oils.

Radiation Polymerization in the Presence of Catalysts

An investigation of the effect of Co^{60} γ radiation on the induction of polymerization in the presence of a chemical-free radical catalyst has been undertaken. The polymerization of styrene monomer with a combination of Co^{60} γ rays and benzoyl peroxide is being studied.

This combined system offers several economic advantages over the individual systems now being used. In this manner, radiation dose requirements could be reduced, initiation of catalytic induction at low temperature is possible under safer conditions, and the molecular weight of the polymer product could be controllable.

Polymerization rates for styrene have been obtained with the combined system at 20°C and compared with the rates obtained with γ rays alone. The experiments were performed at a radiation intensity of 2.6×10^5 rads/hr and benzoyl peroxide concentrations ranging from 0.2 to 5.0% by wt. In each case where benzoyl peroxide was used, an appreciable increase in polymerization rate (amounting to as much as a factor of 4) has been observed to date.

In the combined system, the γ rays not only serve to initiate styrene free radicals but also serve as a "trigger" for the decomposition of benzoyl peroxide to form free radicals. The combined effect of both of these types of free radicals results in a polymerization rate that is higher than that obtained by the individual systems at 20°C .

It should be noted that the temperature range normally used for the decomposition of benzoyl

peroxide for initiating polymerization reactions is $\approx 70^\circ$ to 100°C . Below these temperatures the peroxide is inefficient, and at room temperature it is quite stable with a decomposition half-life of $\approx 60,000$ hr.

Some of the significant conclusions resulting from this work are:

1. Radiation can be used in combination with chemical catalysts to increase the rates of reactions for polymeric and other systems. This is an area of study that has not been reported in the open literature.

2. The use of radiation as a "trigger" for the decomposition of chemical catalysts greatly increases the effective temperature range to which a catalyst such as benzoyl peroxide is limited. It is conceivable that extremely low radiation intensities are required to effectively decompose the peroxide catalyst. It is also conceivable that the radiation intensity, which is a governing factor in the decomposition rate of benzoyl peroxide, can be varied to control the polymerization rates of monomers at low temperatures to produce a more homogeneous polymer.

3. Since the properties of polymers, such as molecular weight and molecular weight distributions, are largely dependent on polymerization temperatures, the increased operating temperature range of a catalyst such as observed experimentally can result in a wider range of polymer properties including that obtained with thermal-catalytic processes practiced commercially.

Further work with this combined system will involve effects of temperature on polymerization rates of styrene up to temperatures where decomposition of benzoyl peroxide is thermally induced.

Cryogenic Radiation Chemistry

In view of the ever increasing interest in cryogenic reactions as a way to improve production of existing industrial chemical products and to synthesize new and unusual products as well as the ability to use γ radiation *in situ* for the generation of free radicals or active species, an experimental system has been constructed with which to perform experiments with radiation at temperatures between -195° and -150°C and pressures to 69 atm in a static stainless steel reaction vessel. Liquid N_2 is maintained in the Dewar surrounding the glass-encapsulated reaction vessel by an automatic filling device actuated by a nitrogen-filled probe attached to a pressure-sensitive switch. The

temperature is controlled by the addition of a small amount of power to stainless steel sheathed Nichrome windings surrounding the vessel. A solid-state power proportioning cryogenic temperature controller is used in the apparatus.

Initial experiments have been performed with N_2 - H_2 mixtures. One experiment was performed at $-160^\circ C$ and 40 atm with the reaction vessel filled with liquid N_2 - H_2 (7% H_2). After 19 hr at 3.15 Mrad/hr, the ammonia concentration was 340 ppm in the 16 g of liquid for a G -value of 0.33. Experiments will also be conducted in the gaseous state at low temperatures and with solid additives.

NEW SYSTEMS

During the course of the year several interesting reactions have been proposed by various groups for investigation with Co^{60} γ radiation. These include the following:

1. The reaction between NH_3 and CO for synthesis of formamide. The idea here is that an alkaline catalyst is used in the conventional thermal process which requires that a costly purification step for removal of impurities such as CO_2 from CO be employed prior to the catalytic reaction step. Also the lifetime of the catalyst is short and this constitutes a costly item in the process. It is hoped that Co^{60} γ radiation induction would eliminate the need for a catalyst and at the same time eliminate the need for high purity CO. Experiments along these lines are under consideration.

2. The reaction between H_2 and CO for formaldehyde and methanol. The synthesis of formaldehyde by photolysis of mixtures of H_2 and CO is well known. However, the yields and efficiency of utilization of the photolytic energy in production reactors are relatively low. It would be interesting to determine the yields by Co^{60} γ radiation induction, since these reactions and products are of great industrial value.

M. STEINBERG

Radiation Chemical Engineering

F. HILL

Theoretical and experimental investigations are conducted on radiation chemical reactor performance with the objectives of providing a framework for the design and scale-up of radiation chemical reactors and for the interpretation of experiments on the kinetics of radiation chemical reactions.

MIXING AND DIFFUSION EFFECTS IN CHEMICAL REACTORS

In earlier work it was shown that mixing or diffusion tends to enhance the performance of reactors in which the initiation rate distribution is spatially nonuniform. This result was obtained for two separate situations: for reactant mixing in s th order ($s \geq 0$) reactions at all conversion levels, and for mixing of chain carriers at small conversions in chain reactions with termination via mutual reaction of chain centers. The result holds for batch reactors and for tubular reactors with arbitrary residence time distributions.

This work has now been extended to include the combination of the two situations. Thus, it has been shown that for chain reactions which are s th order with respect to reactant and for which chain termination occurs by mutual reaction of chain centers, the introduction of mixing in the direction of initiation rate nonuniformities results in enhancement of reactor performance. Four idealized mixing cases are conceivable corresponding to combinations of the two extreme rates of mixing—no mixing (NM) and perfect mixing (PM)—of reactant and chain centers. The case involving the PM state for chain centers and the NM state for reactant is not likely to be encountered in practice. Of the remaining three the case most likely to be found is that involving the PM state for reactant and the NM state for chain centers.

In previous calculations on the effects of diffusion in nonuniformly initiated chain reactions numerical instabilities were encountered in the region of small diffusivity and large optical density. This limiting situation is of intrinsic mathematical interest and is necessary for the complete representation of a reactor model. Furthermore it is the situation often met in practice. During the past year a singular perturbation solution and a point source solution of this problem were obtained. Also an approximate solution valid at large diffusivities was found. R. FELDER, L. SHENDALMAN*

RADIATION-INDUCED POLYMERIZATIONS IN CONTINUOUS STIRRED TANK REACTORS

A theoretical study of the performance characteristics of continuous stirred tank reactors when used to conduct radiation-induced polymeriza-

*Research collaborator, Yale University.

Figure 11. Molecular weight distribution function, w , vs j , chain length in monomer unit. Reactor is 4 ft in diam $\times$ 4 ft high with an axial line source of Co^{60} γ radiation with a source strength of 100 Ci/cm. Source well diameter is 3.25 in. PM = perfect mixing of chain centers; NM = no mixing.

tions has been carried out. Effects on conversion and molecular weight distribution of the interaction of radiation attenuation, chemical kinetics, and mixing were examined for initiation by ultraviolet light and by Co^{60} γ radiation of the bulk polymerization of methyl methacrylate. Direct photoinitiation and photosensitized initiation were considered in connection with the use of ultraviolet light. Two states of mixing of the propagating species were assumed corresponding to chain lifetimes that were long (PM) or short (NM) compared with the reactor mixing time.

In the direct photoinitiation mode, small optical thicknesses and long chain lifetimes were found, whereas with photosensitized initiation, large optical thicknesses and short chain lifetimes existed. Intermediate values were found for Co^{60} γ radiation.

In each initiation mode the transition from the NM to the PM state resulted in increased fraction conversion, increased number average chain length, and decreased weight average chain length. The magnitude of the optical thickness determined the relative effect of mixing state. Large values of the optical thickness corresponded to a large mixing effect and vice versa. Mixing effects on molecular weight distribution are illustrated in Figure 11.

The radical lifetime relative to the mixing time determines which mixing state is significant in practice. A high intensity source yields a short radical lifetime corresponding to significance to the NM state. The opposite result would follow for a low intensity source.

Polymerization reactor performance may thus vary considerably with optical thickness and radical lifetime which are characteristics in part of the initiation mode used.

From a design viewpoint it is important to estimate reactor performance using the NM equations when the radical lifetime is short and the optical thickness is large. When τ is small, the PM equations would probably be used regardless of the magnitude of the radical lifetime, since there is little effect of mixing state and the PM calculation is simpler to carry out. It is also important to realize that at high optical thicknesses and short radical lifetimes a limiting production rate will be encountered as the reactor is made larger. This limiting rate can only be overcome by increasing the source intensity.

H. CHEN*

THERMAL STABILITY OF A PHOTOINITIATED CHAIN REACTION

An initial theoretical effort on this topic has been completed. It may be summarized as follows.

For chain reactions with biradical termination, the Frank-Kamenetskii conductive theory of thermal ignition was extended to include the explicit spatial dependence arising from nonuniform photoinitiation. Novelty in the work included consideration of the small activation energies characteristic of photoinitiated chain reactions as well as consideration of nonuniform initiation. As in other problems involving nonuniform initiation, the presence of nonuniform initiation requires inclusion of mass diffusion or mixing as a process cooperating in the determination of the property of interest, namely, thermal stability.

Calculations were made for low conversions in a slab reactor with Lambert's law attenuation of radiation from a source. The temperature distribution, which is no longer symmetrical about the midplane, has its maximum between the midplane and the source. The skewness is greater, the greater the optical thickness and the smaller the diffusion rate, and the greater the skewness, the more stable the reactor is against thermal ignition. A profile of the concentration of chain centers and the corresponding temperature profile for an optically dense reactor with little diffusion of chain centers is shown in Figure 12.

*Research collaborator, Newark College of Engineering.

Figure 12. Typical concentration (C) and temperature (θ) profiles for an optically dense system. Z is dimensionless distance from the radiation source. τ is reactor optical thickness in mean free paths. Profiles were calculated for an intermediate diffusion rate and for a stable state close to instability.

In many practical instances, strong free convection currents will be present which are not accounted for in the calculations. In this situation, when the conductive theory predicts stability, the prediction will be conservative. Instability cannot be reliably predicted without a further extension of the theory to account for the presence of free convection.

L. SHENDALMAN

INFLUENCE OF FLOW REGIME ON THE PERFORMANCE OF A CONTINUOUS TUBULAR RADIATION CHEMICAL REACTOR

The performance characteristics of a continuous tubular radiation chemical reactor employing an isotopic source of β particles have been investigated. In particular, when using a chemical dosimeter solution as the reactant, measurements have been made of conversion vs mean residence time in laminar flow and in turbulent flow.

An annular reactor made of glass and resembling a chemistry laboratory condenser was used in the experiments. A 20-Ci Sr^{90} - Y^{90} β line source was placed in the central tube, and the reactant passed through the outer, annular shell. The active length of the source was ≈ 30 cm. The reactant annulus dimensions were 30 cm long $\times$ 0.46

Figure 13. Fraction conversion, f , vs dimensionless mean residence time, θ , for continuous tubular reactor with β -particle source. Reaction is the oxidation of 0.001 M ferrous sulfate in air-saturated 0.8 N H_2SO_4 solution. (a) Single-pass laminar flow. (b) Turbulent flow with recirculation.

cm i.d. $\times$ 1.55 cm o.d. Air-saturated Fricke dosimeter solution (0.001 M ferrous ammonium sulfate in 0.8 N sulfuric acid) was used as reactant. For experiments in laminar flow, the reactor was arranged in a once-through flow system. In the turbulent flow experiments, the reactor was made a part of a high flow rate recirculating system that had low flow rate feed and product streams.

Data are shown in Figure 13 in which f , the fraction conversion of ferrous ion, is plotted against θ , the mean residence time in units of the mean chemical lifetime. Figure 13a is for the single-pass system and Figure 13b is for the system with recirculation. The data obtained were fraction conversion as a function of mean residence time (based on net flow rate in the recirculating system). The initial slopes of the theoretical and experimental relationships were matched by applying a scale factor to the experimental mean residence time values.

The solid curves in Figure 13a are theoretical curves for the two extremes (PM and NM) of radial mixing in single-pass operation. The two curves represent the solutions of the appropriate differential equations in a tubular flow system. The kinetics expressions of Allen and Rothschild [*Rad. Res.* 7, 591 (1957)] were used in formulating the equations. Implicit in the calculation of the PM curve is the assumption that the velocity and radiation intensity are constant throughout the reactor at their average values. In the NM calculation, at each radial position, the velocity is assumed to be that for fully developed laminar flow, and the intensity is that calculated using Loevinger's empirical expression for an infinite

line source (J. SILVERMAN, *Large Radiation Sources in Industry*, Vol. 1, p. 31, IAEA, Vienna, 1960). The location of the laminar flow data between the NM and PM curves is consistent with the fact that a small but finite amount of radial mixing, in the form of molecular diffusion, is present.

The solid curve in Figure 13b is the theoretical relationship for a continuous stirred tank reactor with the same through-flow rate as the recirculating system, the same reaction kinetics, and the same average intensity. The data fit the theoretical relation well over the entire range of fraction conversion.

The average dose rate can be determined from the scale factor applied to the experimental residence time to match the data to the theoretical curves. The matching is more straightforward in the recirculating mode. C. DAVIS, A. MULLER, M. ROTHBART

BLOOD IRRADIATOR CHARACTERISTICS

A series of experiments to determine the characteristics of an irradiator for the extracorporeal irradiation of blood have been carried out. The irradiator is a small scale prototype with a source of

Figure 14. Experimental version of irradiator with β -particle source for extracorporeal irradiation of blood, manufactured by Atlantic Research Corp.

Figure 15. Distribution of activity along length of blood irradiator.

$\text{Sr}^{90}\text{-Y}^{90}$ β particles, and is manufactured by the Atlantic Research Corporation.

The experimental objectives were to determine the relative dose rate distribution along the source and the mean absorbed dose rate which would be imparted to the blood stream. Figure 14 shows the source with dimensions and the lead shield in which it is transported. The source was reported to consist of about 1 Ci of $\text{Sr}^{90}\text{-Y}^{90}$. The source consists of a Vycor tube impregnated with Sr^{90} -bearing SrCl_2 .

The relative dose rate distribution was obtained by using the method described in BNL 923 (T-380). An 'n' on 'p' solar cell connected to appropriate instrumentation was moved in small increments through the source. The technique and results are illustrated in Figure 15. The distribution of Sr^{90} along the Vycor tube is evidently highly nonuniform.

The mean absorbed dose rate of the blood irradiator was determined by recirculating standard Fricke dosimeter solution through the source at a high flow rate, while pumping a very small net flow through the system. Silastic tubing of the same type and dimensions (0.114 in. o.d. $\times$ 1.110

Figure 16. Fraction conversion vs reciprocal through-flow rate in ferrous sulfate oxidation carried out in blood irradiator.

in. i.d.) as that used in medical applications was used in the irradiator. The tubing was slightly smaller than the i.d. of the irradiator, and could not be kept centered while running, so that a slight deviation from the maximum mean absorbed dose rate probably resulted. Figure 16 shows the experimental points obtained and the mean dose rate curve drawn as the best straight line from the origin through them. The mean absorbed dose rate in the flowing solution is calculated as 71,450 rads/hr in the 0.49 cm^3 of tubing in the active source or, in units convenient for medical purposes, 5.84 rads/pass at a flow rate of 100 ml/min.

Attempts were made to operate the apparatus in laminar flow in order to get an indication of the effect of flow regime on the mean absorbed dose rate. The very low flow rates required to get significant conversions, because of the low source strength, could not be maintained constant for a long enough period of time (with the equipment available) to achieve steady state. Indications were, however, that the laminar flow points would fall below the line shown in Figure 14.

A. MULLER,
C. DAVIS, J. EICHACKER, M. ROTHBART

GAMMA REACTOR STUDY

A number of experiments have been carried out on the performance of a radiation chemical reactor in which the radiation is emitted by a Co^{60} source. A summary of the findings is given below.

The reactor studied was a continuous stirred tank reactor, 6-in. in diam $\times$ 12 in. high. It was made of glass with a central well for a strip source of Co^{60} . A stirrer, also of glass, with two marine-type impellers on the same shaft was located in the annular reactant volume.

Standard air-saturated Fricke dosimeter solution was used as reactant. The solution was supplied to the reactor from a glass constant head tank, and the flow rate was controlled by means of a throttle valve.

In the experiments, the fraction conversion of ferrous to ferric ion was determined as a function of reactant flow rate, with stirrer speed and source strength as parameters.

The relation between fraction conversion and mean residence time which might be expected from such a reactor is bounded by two limiting relations that correspond to two extreme types of mixing models. In one such type of model, mixing is complete down to the molecular scale and is referred to as "complete micromixing." In the other, the reactant on entering the reactor is dispersed into "clumps" which retain their identity during passage through the reactor. The clumps are large compared with the scale of molecules and small compared with the scale of the reactor. The flow in this case is said to be "completely segregated." Both the molecules in the case of complete micromixing and the clumps in the case of complete segregation have the same residence time distribution, namely, that expected of a perfectly mixed continuous tank reactor. The two limiting relations are shown in Figure 17. The ordinate is fraction conversion, and the abscissa is a dimensionless mean residence time defined by

$$\theta = (GIV)/(C_0AF),$$

where $G = 0.156$ molecules Fe^{+3} produced /eV absorbed,

$I =$ mean absorbed intensity, eV/liter-sec,

$V =$ reactor volume, liters,

$C_0 =$ influent reactant concentration, 0.001 mole/liter,

$A =$ Avogadro's number, and

$F =$ flow rate, liter/sec.

The curves were calculated taking into account the mixing state, and the kinetics and rate constants of the ferrous sulfate oxidation as given by Allen and Rothschild (*op. cit.*). Mixing state is of little consequence at small conversions; at high conversions larger effects are found.

Figure 17. Fraction conversion vs dimensionless mean residence time in continuous stirred tank reactor with axial Co^{60} γ source.

The data obtained were plotted on the same coordinates. For the data obtained at a given source strength, the abscissa was defined as $\theta = k/F$, and the constant k was chosen such that the initial, straight line portion of the curve defined by the data coincided with the initial linear portion of the theoretical curves.

All of the data agree well with the complete micromixing curve up to a fraction conversion of 60%. Beyond this point some segregation seems apparent. No effect of stirring speed is evident with the 676-Ci source. Stirring speed has a significant effect with the 2450-Ci source. At 2200 rpm the data for the higher strength source are in agreement with those for the other source.

The average dose rates and reactor efficiencies deduced from the data are 126,000 rad/hr and 16.6% for the 676-Ci source, and 417,000 rad/hr and 15.1% for the 2450-Ci source, respectively.

P. FALLON

EFFECTS OF MIXING ON A NONUNIFORMLY INITIATED PHOTOPOLYMERIZATION

In these experiments the rate of a photopolymerization carried out in a partially illuminated, agitated vessel is measured as a function of stirrer speed. Direct photoinitiation was used with light of wavelengths from 3000 to 4000 Å. A series of experiments were conducted in each of which the rate was measured as a function of time at constant stirrer speed. A slow decrease of the rate with time was found after passing through an induction period. The rate at zero conversion was determined by extrapolation to the start of illumination. The initial rates so measured varied erratically with

stirrer speed. Spectrophotometric studies of the reactant before and after irradiation suggested the presence of one or more spurious initiators. A change in monomer purification procedure eliminated the spectral evidence of spurious initiators but also resulted in inconveniently low reaction rates. Photocatalysts will be tried in future experiments.

J. EICHACKER, A. MULLER

THE RADIATION-SENSITIZED QUARTZ DOSIMETER

A new type of quartz dosimeter suitable for use in the 5- to 50-krad range is under development. The dosimeter is produced by exposing a plate of very pure fused or natural crystalline quartz to a large dose (10^8 to 10^9 rad) of Co^{60} γ radiation. The irradiation is followed by an annealing treatment at a temperature between 200° and 400°C for a period of ≈ 24 hr. At this point the dosimeter is ready for use.

The irradiation and annealing sequence results in the introduction of a controlled number of defects into the crystal lattice and the development of a stable ultraviolet absorption band upon subsequent exposure to Co^{60} γ radiation. The number of defects is proportional to the magnitude of the sensitizing dose.

The peak of the absorption band is located at a wavelength of $215\text{ m}\mu$, and the absorbance at this wavelength increases linearly with dose over the range 5 to 50 krad. As an example, the response of an Amersil fused quartz dosimeter to Co^{60} γ radiation is represented in Figure 18. This dosimeter was sensitized with a dose of 5×10^8 rad followed by a 24-hr annealing treatment at 350°C . The dosimeter was then irradiated in increments of 5 krad to a total dose of 90 krad. The absorbance was measured after each irradiation. The resultant absorbance change is plotted vs total Co^{60} γ dose. The response is linear at doses up to 50 krad at the rate of 0.0026 absorbance change per kilorad. Saturation begins to set in above 50 krad. The response of untreated Amersil quartz, also shown in Figure 18, is lower than that of the sensitized material by more than an order of magnitude.

Bleaching rates have been found to be of the order of one percent per month at room temperature. No dose-rate dependence has been found. Although energy-dependence tests have not yet been made, the low atomic numbers of the quartz constituents should tend to minimize this variation. By contrast, other glass coloration dosimeters,

Figure 18. Response at $215\text{ m}\mu$ of sensitized and unsensitized Amersil quartz (Infrasil grade) to Co^{60} γ radiation. Sensitizing dose, 5×10^8 rads; temperature, 350°C ; time, 24 hr.

which are sensitized by the addition of high-Z additives such as silver or cobalt, show marked energy-dependence.

In addition to its general usefulness in the low dose range, the quartz dosimeter may be useful as a particulate tracer-dosimeter in flow systems. It is resistant to physical and thermal shock, and its hardness (Moh's scale 5-7) may preclude the need for a protective covering. The dosimeter dimensions are $\frac{1}{4} \times \frac{5}{8} \times \frac{1}{16}$ in. thick. These dimensions were chosen to be compatible with absorbance measurements in a standard Beckman DU spectrophotometer.

A. MULLER

Radiation Engineering

J. CUSACK

HIGH INTENSITY RADIATION DEVELOPMENT LABORATORY OPERATIONS

Source Inventory

Source inventories maintained or on order for research and development activities included, at the end of the year, $> 2.5 \times 10^6$ Ci Co^{60} ranging from 0.1 to 500 Ci/g in specific activity and from 10 to 9000 Ci in individual source strengths; 400,000 Ci Cs^{137} ; and 1100 Ci Sr^{90} . Major inventory changes this year involved the acquisition (from SRP) and secondary encapsulation (by Lockheed) of 500,000 Ci Co^{60} in 94 Mark II bonded sources; the receipt of the first 1100 Ci of a new BNL/ORNL developed Sr^{90} source; the recovery, repair, and re-encapsulation of several

hundred thousand curies of corroded, damaged, and initially rejected Co^{60} sources; the developmental encapsulation of about half a million curies of very high specific activity ($>500 \text{ Ci/g}$) Co^{60} sources; and the acquisition of sufficient Mark I Cs^{137} sources ($>360,000 \text{ Ci}$) to allow large plaque irradiations.

Cell Activities

The preparation cell was operated at near capacity on a single-shift basis. Example operations include calorimetry and assay of megacurie quantities of cobalt and cesium; the development and use of specialized remote welding equipment for the secondary encapsulation of cylindrical sources; the remote loading of numerous units including the Portable Cesium Irradiator, the Shark Brain Irradiator, and a blood irradiator; and the remote examination and de-encapsulation of badly corroded Co^{60} sources.

The radiation cell was also operated at near capacity on a single-shift basis. Example operations this year included the irradiation of numerous monomer-loaded concrete test specimens; measurement of γ dose distributions in food can phantoms to develop design data under the IRRADCO contract; verification of IRRADCO design data utilizing a specially constructed mock-up of the IRRADCO conveyor system; and the fabrication and operation of a continuous flow, γ -irradiated liquid system in support of reactor vessel design research. Continuing basic research conducted in the cell included cesium-cobalt comparisons and dose distribution studies in homogeneous and heterogeneous targets.

Table 4

Use of Gamma Facility for Period
October 1967 to October 1968

User	Sample hours
Nuclear Engineering Dept.	39,884
Physics Dept.	3,565
AGS Div.	3,128
Biology Dept.	146
Chemistry Dept.	126
Off-site	13,241
Total sample hours	60,090

There were 3526 samples irradiated in 1380 separate irradiations.

GAMMA FACILITY

A new underwater γ facility has been completed which provides carefully calibrated cobalt γ dose rates from 5×10^3 to 10^7 rad/hr . During the past year about 5000 sample hours of irradiation were performed each month in either the old or the new facility (see Table 4). Use of the underwater γ facility is expected to grow as the availability of standardized, reproducible cobalt γ dose rates becomes known to researchers. Expansion of this capability to include cesium, and possibly strontium, is planned for 1969.

GENERAL ENGINEERING PROGRAM

HIRDL Conveyor System

It had been anticipated that advances in food irradiation technology would lead to requests for the pasteurization or sterilization of large test lots of various foods in support of USAEC and DOD programs starting in the summer of 1968. Consequently, a reconstruction of the HIRDL continuous conveyor system was completed so that such tasks could be accomplished with minimum manpower and maximum useful data generation. Unanticipated delays in Food and Drug Administration clearance procedures will apparently postpone large quantity processing. When required, however, the redesigned facility will be capable of the cesium or cobalt irradiation of multi-ton lots in a choice of operational modes: (1) intermittent cross-feed, (2) two-pass, one-plaque, or (3) one-pass, two-plaque.

Expansion Plans

The capacity operation of the two HIRDL cells has, with increasing frequency, led to experimental priority problems. The inefficiency of tying up one of the large cells with experiments or operations which could better be accomplished in smaller, more flexible cells is particularly noted. Consideration of this problem, together with the anticipation of new or changing facility requirements in the future, resulted in initiation of an over-all HIRDL facility study. A set of recommendations, including preliminary plans and cost estimates, for a HIRDL rebuilding program is to be issued early next year. To date, the major requirements appear to be increased laboratory and operations areas and two small, intermediate level hot cells.

Irradiator Design

Based on experience gained by the fabrication of the first Brookhaven Portable Cesium Development Irradiator (BPCDI) unit, minor design improvements have been made and will be incorporated in the second and third units.

Because of new Department of Transportation (DOT) requirements concerning the safe shipment of radiation sources, the AEC-owned Portable Cesium Irradiator (PCI) must be remounted in a new and more extensively braced trailer. The trailer has been designed in cooperation with a vendor and is now under construction. Based on the experience gained and difficulties encountered by Isotopes, Inc., in its operation of the PCI, certain features of the unit were redesigned and will be rebuilt during the trailer change.

As part of the BNL support to the AEC-IRRADCO meat irradiator pilot plant design, the IRRADCO design concept was mocked-up in the HIRDL irradiation cell utilizing an automatic indexing, four-position conveyor. Use of this device with BNL standard Mark I sources and with the Neutron Products, Inc., sources selected for the plant allowed the prediction of dose distributions to be anticipated in the IRRADCO four-pass, single-slab quadrant irradiator.

A portfolio of concepts, varying in degree of completeness, is being prepared to anticipate foreseeable requirements. Concepts, tentatively scheduled for preparation, include a mother ship irradiator for the shrimp industry and a can irradiator designed to utilize ultra-high specific-activity cobalt.

Radiation Damage

A survey and a reassessment of radiation damage studies applicable to γ processing are being made. An organized experimental program to fill in current gaps in damage knowledge will be instituted. The goal is the publication in fiscal year 1970-71 of a reasonably comprehensive manual on radiation damage to serve as a guide to facility designers and users.

COMPUTER CODES

Modifications

Modifications of existing γ codes to broaden their utility continued this year, including the following.

The QAD-5 program computes γ dose rates from a finite cylindrical source. The program was modified to make it simpler to use for a large number of detector points and to more accurately account for self-absorption effects at target points close to the source by means of a nonuniform stepping function based on the sum of an arithmetic progression. The accuracy of the program was verified, and it was used for a series of sodium pipe source calculations.

The GOLF-P was modified to permit parameters such as source size, target density, source-to-target air gap, and source type to be treated as variables using a simplified input.

Code Application

The various codes were extensively used (a) in support of AEC-IRRADCO pilot plant design studies, (b) to predict source placement for optimum uniformity when fueling such units as the University of Florida Research Irradiator and the foreign loan BPCDI's, and (c) to calculate the static dose distributions throughout chemical irradiators.

Tables of data were prepared and published together with appropriate instructions to permit quick and easy dose distribution calculations for preliminary design of cobalt and cesium irradiators.

Beta Dose Distribution

A calculation is now being completed of the β dose rate from a rectangular β source plaque in a homogeneous medium, taking into account the effect of source self-absorption.

The prediction method, although not a Monte Carlo calculation, makes use of routines developed for Monte Carlo codes. This method depends upon the assumption that small angle scattering is overwhelmingly important and that the actual path length traversed can be considered the depth of penetration. This method is thought to be accurate enough yet simple enough for use in predicting the strength of some prospective β sources. It will be tested against more conventional (Monte Carlo and other) types of calculations.

Comprehensive Design Code

The preparation of an integrated, comprehensive γ irradiator code is continuing. The perhaps idealistic goal is a "push-button" code yielding maximum design information yet requiring minimum knowledge and experience on the part of the

designer. Those code aspects that are now semi-empirical in nature (e.g., dose buildup) will be reassessed on a theoretical basis in an attempt to develop more rigorous predictive techniques.

SOURCE DEVELOPMENT

Source Assay

Improvements in the adiabatic calorimeter and the assayer have assured reliability and reproducibility of activity measurements. Designs were supplied to SRP and ORNL.

Co⁶⁰ Radiation Sources

The forty-eight Hawaiian Development Irradiator Mark I cobalt sources that failed were reclaimed by specially developed procedures. Corrosion caused failure during shipment to and from Hawaii. Improved source holders and shipping techniques proved effective for replacement sources. Cladding failure, due to entry of sea water into the shipping cask, is being analyzed by synthesis. Apparatus developed for this purpose will also be useful in testing new cladding materials.

The Mark I cobalt source, shown to be satisfactory when fabricated by following specifications exactly, is safe to use in environments noncorrosive to 316L SS. The Mark II source is even more reliable because of its metallurgically bonded encapsulation. More economical activation is gained by elimination of additional in-reactor encapsulation. Disadvantages, compared with Mark I sources, are lower cobalt weight and sophisticated fabrication techniques. The nondestructive dye penetrant continuity test was modified to give correct results on Mark II slabs. The Mark II, successfully activated, is considered commercially acceptable.

The first batch of Mark III sources was fabricated identical to Mark II sources, but with the cobalt weight raised to the Mark I value and with cladding thickness reduced. Investigation commenced of other cladding techniques, including explosive forming and electrodeposition of niobium and of nickel. Also started was the investigation of corrosion resistant cobalt alloys to replace pure cobalt cores.

Special problems involved in secondary encapsulation and use of ultra-high specific activity cobalt (>500 Ci/g) were investigated. Neutron

Products Corp. rod and spiral sources were procured and encapsulated, and are under evaluation.

Cs¹³⁷ Radiation Sources

Development of the Mark I cesium source continued. Cracks, found along the internal corners of the source envelopes, could propagate under excessive stress. Swelling, occurring occasionally under high temperature, was traced (by ORNL) to impurities in CsCl and eliminated. Mark I cesium sources are not recommended now for frequent in-out pool operation.

Requirements for advanced cesium source types (Mark II, etc.) are being assessed, and design and development will be initiated as indicated. Possible advantages of high ratio 134/137 cesium sources are being investigated. If warranted, ORNL will be requested to make a small number of such sources for evaluation.

Sr⁹⁰ Radiation Sources

Dummy Sr⁹⁰ sources, of the stainless steel encapsulated, strontium silicate aluminum matrix design, were supplied by ORNL and evaluated. At ORNL radioactive strontium silicate microspheres were made, loaded, and sealed into stainless steel sheaths.

Proof testing of these moderate efficiency, high integrity β sources is planned. Development of potential uses, especially in the areas of fluid irradiators and surface treatment (e.g., meat pasteurization), is expected to accelerate. The resultant generation of source parameter requirements will be met by long-range source development similar to the now matured cobalt program. By year-end, specific goals and time requirements for such developments should be reasonably well defined.

Cycling Tests

Pool-air cycling tests suggesting low stainless steel corrosion rates will be accelerated by addition of automated cycling apparatus late this year.

DOSE DISTRIBUTION STUDIES

Pilot Plant Application

Because of the intense interest in the AEC/IRRADCO pilot plant project, the previously scheduled order of dose distribution studies was altered to stress heterogeneous targets consisting of can arrays.

Experimental equipment was designed and constructed for the irradiation of arrays of No. 10 and No. 3 food cans using a homogeneous source plaque, containing 518,000 Ci, as BNL standard Mark I Co^{60} sources.

Extensive static studies of can arrays were completed using a variety of dosimeters. Dose uniformity ratios were determined for each target arrangement, enabling the selection of arrays yielding acceptable maximum and minimum doses.

The results of these static studies were later verified under dynamic conditions. For this work the IRRADCO irradiator concept was mocked-up in the HIRDL irradiation cell (Figure 19). The concept was a four-pass, single-slab quadrant irradiator with a source plaque 28 in. high and 25.75 in. wide. The mock-up utilized eighteen product

carriers and allowed an 1800-lb target to be automatically indexed through four positions for a total distance of 8.5 ft, dwelling for a pre-set time in each position.

A series of experiments were then conducted to determine differences between BNL Mark I standard cobalt sources and the Neutron Products rod and spiral type sources proposed for plant use. The sources were compared dynamically under conditions of identical geometry, measuring the total dose delivered, at several depths, to rice-loaded No. 10 cans. The results indicated that the BNL Mark I sources give the flattest depth dose distribution and the highest utilization efficiency. Next flattest in dose distribution was the NPI coil source. The difference in source efficiency between NPI coil and rod sources is very slight.

Heterogeneous Targets

In heterogeneous target studies, resumed after a long delay because of the IRRADCO work, the greatest emphasis is being placed on improving calculational techniques for dose prediction in heterogeneous target systems using extended Co^{60} and Cs^{137} sources. In the initial static experiments, infinite arrays of food cans are being used as the target materials. The diameters of the cans are being varied from 2 to 6 in. and the bulk densities of the arrays vary from 0.2 to 1.0 g/cc.

Dose distributions in these heterogeneous arrays are being compared with FUDGE 4A computer predictions and with dose measurements made in homogeneous targets of the same effective density.

DOSIMETRY AND DOSIMETER DEVELOPMENT

Effects Dosimetry

A study of "effects" dosimetry in grain irradiation initiated last year was continued. It was found that water extracts of Red Western wheat, which was previously treated with methyl bromide (a fumigant commonly used with wheat), possessed an optical absorption spectrum with peaks at 235 and 275 $\text{m}\mu$ which was destroyed by Co^{60} γ irradiation. These peak heights were found to be approximately inversely proportional to the radiation dose administered in the range from 10 to 50 krad (Figure 20). It is probable that the wheat so treated can be used for the calibration of bulk grain irradiators such as the BGI where flow patterns are a complicating factor. Further testing

Figure 19. Dynamic version of IRRADCO Irradiator. Cutaway shows proposed carrier loading.

Figure 20. Absorption spectra of water extracts of Co^{60} irradiated wheat.

of this assumption is now being carried out at the USDA station in Savannah, Georgia.

Dosimeter Stability

Long-range dosimeter stability studies were continued in this period. The dosimeters under test are the Perspex-HX, high and low dose ferrous-cupric, de-aerated and standard Fricke, and the ceric-sulfate dosimeter.

Ferrous Cupric Sulfate Dosimeter

Results of a four-month study of the new high dose ferrous cupric sulfate dosimeter indicate that solutions prepared and sealed in 5-ml ampoules can be kept over this period with no detectable loss in ferric ion yield. These results were found for samples which were pre-dosed to 5×10^5 rads as well as those which were not. The pre-dosed samples were found to be slightly less reproducible than those which were not pre-dosed.

Manual Publication

A chapter has been written for a textbook entitled *Manual on Radiation Dosimetry* to be published shortly in Denmark. The chapter is a detailed summary of the proper procedures for performing radiation dosimetry in research and processing, and includes discussions of absolute absorbed dose, dose distribution, and process control measurements. The chapter deals with dosimetry in a wide variety of irradiators and is highlighted by detailed discussions of dosimeter selection criteria for all purposes.

Workshop Activities

The Third Biennial Dosimetry Workshop was held, along with a meeting of the ASTM Dosimetry Sections of Subcommittee D9/D20 on Irradiation of Plastics, at the U.S. National Bureau of Standards, Gaithersburg, Maryland, April 8-10, 1968. The three main topics of discussion were (1) absorbed dose standardization, (2) high intensity and pulsed radiation dosimetry, and (3) new developments in methods and techniques of radiation dosimetry. The ASTM proceedings consisted of setting up the long-range mechanics for writing standard procedures for all the γ and charged-particle dosimeters currently in use. The meetings were attended by seventy-five persons from sixty different establishments representing universities, government agencies, and private companies.

Quartz Dosimeters

Two radiation-sensitized quartz dosimeters were developed. The first, made from Infrasil, shows linear response up to 5×10^9 rads and shows no change in absorbance up to 150°C . The second, made from Optisil, is linear up to 2×10^5 rads and is stable up to 50°C . Each is reproducible under optimum conditions to within 5%. These dosimeters should find wide application in measuring the absorbed dose in high density targets, in monitoring the cumulative dose to electronic and mechanical components inside hot cells, and as dose indicators for process control.

FOOD PROGRAM

Irradiator Support

In support of a contract between AEC-NYOO and Lockheed, BNL is supplying off-site consultation and guidance during the maintenance of AEC-supported pool-type research irradiators. This year "minor" maintenance efforts were monitored at the University of California, the University of Washington, and Massachusetts Institute of Technology. A "major" overhaul was supervised at the University of Florida. In addition to the normal maintenance items covered at the last installation, a complete source plaque change was accomplished with the substitution of a Cs^{137} plaque (114,000 Ci) for the previously used Co^{60} plaque (22,000 Ci). The cesium source spacing in the new plaque was optimized to provide maxi-

mum dose uniformity by using the GIRD computer code.

The Shipboard Irradiator, originally used on board the Bureau of Fisheries vessel *Delaware*, working out of Gloucester, Massachusetts, was completely reworked at HIRDL: a new source plaque was installed, a DOT-approved crash frame fabricated, instrumentation modified, and complete maintenance accomplished. After standardization, the unit was shipped to Iceland (Figure 21) where it was installed under the supervision of a BNL technician.

A second Shipboard Irradiator was removed from the *R.V. Miller Freeman*, working out of Seattle, Washington, and shipped to HIRDL where it received a total rework prior to its emplacement at the University of Nebraska.

The Portable Cesium Irradiator was returned to HIRDL for two weeks to allow the Mechanical Engineering Division to take dimensions for future modifications necessary to comply with new regu-

Figure 21. Modified shipboard irradiator being loaded for shipment to Iceland.

lations pertaining to the transportation of radioactive materials.

A malfunction had occurred in the irradiator while at ORNL prior to its leaving for BNL. At BNL it was determined that the gear that drives the shuttle mechanism had separated from the drive shaft and the shuttle was stuck in the irradiation chamber, thereby preventing the inner door from closing. A hole was drilled in the outer door and a hook was used to withdraw the shuttle. This permitted the inner door to be closed and the necessary repairs to be made. Once the problem was corrected, the hole in the door was plugged and a self-radiograph of the repair was made to insure its integrity.

A Mark IV pool-type research irradiator was received from the vendor and, after complete assembly, checking, and modification as required, was packed for shipment as a loan unit to Pakistan. It is currently anticipated that this unit will be installed early next year under the supervision of a HIRDL engineer.

The first of three Brookhaven Portable Cesium Development Irradiators (BPCDI) was received from the vendor and, after substantial testing and refit, shipped on loan to Argentina for installation under BNL supervision. The two remaining units should be received early next year and will be installed in India and Chile.

A new source holder and Co⁶⁰ sources (10,000 Ci) were provided for the I.V.E.C. installation in Venezuela.

Inter-Facility Dosimetry Standardization

Preliminary preparations were completed for a large-scale "round robin" dose standardization of all USAEC-supported facilities. This study, to be conducted by mail, will involve a two-step calibration. First, the calibration of all spectrophotometers will be performed with carefully prepared and analyzed standard ferric ion solutions. All units will be calibrated with the same solution prepared at BNL. Second, there will be an interchange of dosed Fricke dosimeters between each facility and BNL. Standard ferric ion solution was carefully made, analyzed, bottled, and prepared for shipment. This inter-facility standardization also includes standardizations between BNL and the U.S. National Bureau of Standards.

The Portable Cesium Irradiator was utilized, with the cooperation of Isotopes, Inc., to perform a cross-calibration involving the BNL thermo-

luminescent dosimeter readout unit, the University of Washington, and the Bureau of Fisheries in Seattle, Washington. The results of these calibrations indicate good agreement (within 1.5%) in dose measurements.

Another inter-unit calibration was later arranged between the PCI and the facilities at Oregon State University and showed similar results. Cross-calibrations of this type will be arranged each time the PCI schedules a stop near an AEC facility.

Facility Calibration

During this period a complete source plaque change was made in the University of Florida Research Irradiator; the unit, originally Co⁶⁰ fueled, now contains a Cs¹³⁷ plaque. Two complete standardizations of the irradiator were performed by BNL personnel – one before and one after the plaque change. The tasks performed were the calibration of the University's spectrophotometer and dose distribution studies in the product carriers used for AEC-supported projects.

BNL personnel visited the HDI and the University of Hawaii facilities during this year to measure dose rate distributions in detail within products such as papayas, mangos, and potatoes. At the Hawaiian Development Irradiator, radiation levels were varied from a dose of 7000 rads to inhibit sprouting in potatoes, to a disinfestation dose for papayas and mangos of 15,000 to 20,000 rads; and to a shelf-life extension dose for papayas of about 100,000 rads. At the University of Hawaii measurements were made throughout the target box both in air and papayas and mangos.

Both the standard Fricke and the ferrous cupric sulfate chemical dosimeters were employed. All solutions and calibrations were made in Hawaii. The location of maximum and minimum dose was obtained for each product at both facilities for typical source and target configurations.

The Shipboard Irradiators previously located in Gloucester, Massachusetts, and Seattle, Washington, were completely calibrated at BNL prior to their new assignments in Iceland and at the University of Nebraska.

Facility standardizations will be simplified and the accuracy of the results improved by the availability of the new underwater γ facility at HIRDL. The combination of this carefully engineered set of irradiation ports with the in-house dosimetry

competence should allow an unprecedented confidence in standard dose determinations.

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Atmospheric Sulfur Pollutants Program

This program is concerned with the behavior of atmospheric sulfur compounds from their point of emission to their ultimate fate. The major emphasis of the program thus far has been on the development of the Isotope Ratio Tracer (IRT) method as a means of unambiguously relating pollutant sulfur compounds to a specific source in a multi-source area, and of tracing their movement through the atmosphere. This technique will make possible experimentation on some of the significant meteorological problems involved in the behavior of sulfur oxides released into the air over large metropolitan areas.

The IRT method depends upon the fact that the ratio of S³² to S³⁴ in the sulfur contained in fossil fuels varies markedly with the nature and source of the fuel. The constant ratio of S³² to S³⁴ in meteoritic sulfur, 22.210, is taken as the standard. Measured ratios are related to it, expressed as either higher in S³⁴ (+ δS^{34}) or lower (– δS^{34}) than the standard, in "per mil" units or parts per thousand. Provided that the S³²/S³⁴ ratio in the fuel being burned in a plant under study is sufficiently different from that of the "background" sulfur in the area, measurement of the stable isotope ratio in samples of sulfur collected from the atmosphere will permit the tracing of the sulfur emitted from the plant. With a precision of ± 0.2 per mil attainable in the isotope ratio mass spectrometer in use and a spread of about 10 per mil between the sulfur ratio in the fuel being traced and in the background, ≈ 1 part of tracer sulfur can be detected in 50 parts of background sulfur.

Samples of atmospheric background sulfur have been collected in several areas, including New

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York City, New Haven, Long Island, and western Pennsylvania, both at ground level and aloft. The S^{32}/S^{34} ratio in general has ranged between +3 and +8. Several fuel oils, both domestic and foreign, have been found with per mil values as low as -9.8 and as high as +14.5, providing an adequate spread.

A high-flow filter pack for collecting both sulfur oxides and particulates from the air has been thoroughly field-tested and is now in routine use with an efficiency of 95%. It is being used for both ground-level and airborne sampling. The method for removing the sample collected on a filter, converting it to SO_2 , and preparing it for introduction into the mass spectrometer has been demonstrated to provide a yield of at least 95% across each step, insuring isotopic integrity. The isotope ratio mass spectrometer designed and built for this application by Nuclides Corp. required considerable effort initially to get it to perform satisfactorily, but since starting up, it has been in regular use and

has given very little trouble. Samples have been cross-checked with the laboratories experienced in measuring sulfur isotope ratios at McMaster University and the University of Utah, with satisfactory agreement. To date, about 70 fuel samples have been processed and about 140 atmospheric samples of both stack plumes and backgrounds.

Experimental work has been started in New Haven with the cooperation of the local power company, United Illuminating Co., with the object of developing air pollution patterns from a small number of major sources under various meteorological conditions. The data obtained will be used to verify the results of a mathematical model that has been developed for the problem. A series of coordinated runs are being carried out at different times of the year and over 24-hr periods to establish seasonal and diurnal variations in the background. Sulfur oxide is collected from the air at three ground stations and aloft both in the stack plume and away from it. Fuels in use at the

Figure 22. Air view of Keystone Power Plant, Indiana, Pa. The aircraft, using the BNL filter pack, is collecting samples of sulfur oxides from the stack plume.

English Station power plant and elsewhere in the area are also sampled. A survey has been made of the city for the other major sources of SO_2 , with the assistance of the New Haven Health Department's Air Pollution Section.

A similar program in New York City has been delayed by the greater complexity of the problem but is now under way with the cooperation of Consolidated Edison. A "tall-stack" power plant on Staten Island, Arthur Kill Station, has been selected as the one most nearly meeting the requirements for a major meteorological experiment in the metropolitan area. A start has been made in assessing the problems involved in such an experiment, both for the operating utility and for the experimental group. The initial study will be of the effectiveness of tall stacks under inversion conditions; whether the stack effluent is able to "punch through" the inversion layer or whether it is contained, with subsequent fumigation of the area.

A cooperative effort is under way with the U.S. Public Health Service's Large Power Plant Effluent Study (LAPPES) being carried out at the Keystone plant of the Pennsylvania Electric Company at Indiana, Pennsylvania. Filter samples are being taken aloft with simultaneous recordings of temperature, altitude, and SO_2 concentration by a conductimetric method. Figure 22 shows the plant as seen from the plane collecting samples of the stack plume. Air samples will also be collected for the National Center for Air Pollution Control and sent to them for analysis, when SF_6 tracer runs are made. Design and construction of the SF_6 injection and sampling equipment are being undertaken by BNL. Since the filter pack used for atmospheric sulfur collection is capable of discriminating between SO_2 and SO_3 , it should be possible to use the Keystone data to determine the rate of conversion of SO_2 to SO_3 under actual conditions in a plume from a coal-fired plant. A similar experiment is being carried out on Long Island at the Northport Station of the Long Island Lighting Company to determine the half-life of SO_2 in the plume from an oil-fired plant.

Exploratory Research & Development

THE PLASMA BETATRON ACCELERATOR

The plasma betatron differs principally from the conventional (high vacuum) betatron in that ion-

ized gas (a plasma) in the doughnut-shaped acceleration chamber is the source of the accelerated electrons, rather than a thermionically emitting filament-electron gun. The advantage of the plasma betatron is that the plasma acts as a prolific source of electrons, theoretically giving rise to circulating currents several orders of magnitude greater than those obtainable from a thermionical device. However, in the brief time in which the plasma betatron concept has existed (≈ 10 years), the achieved values of current, while impressive, have fallen far short of expectations. The matter is of great importance, because a plasma betatron that even modestly fulfills its theoretical design specifications would have immediate applicability in several diverse areas:

(1) As an intense source of γ rays or β particles suitable for industrial irradiation at costs that are highly competitive with those of other types of accelerators; also, via (γ or β, n) reactions, of pulsed neutrons, for example, for the triggering of high-intensity pulsed reactors.

(2) As a research tool or model for studying collective effects in high-intensity, very high-energy particle accelerators being planned, built, or modernized.

(3) A comparatively prolific source (compared with other proposed schemes) of light in the far ultraviolet (via synchrotron radiation).

(4) An experimental device for generating plasmas for thermonuclear and other research.

(5) A device capable of simulating certain nuclear weapons effects.

The promise held by the plasma betatron has led us to the analysis of the few reported experiments. Their failure, insofar as can be established from published reports, surprisingly turns out to be due to either one or both of two reasons: the lack of stable particle orbits in these devices, and the lack of adequate means of preparation of the plasma prior to the acceleration cycle. Moreover, in many instances the experimenters' interests were less in the plasma betatron itself but rather in a means to an end perhaps achievable in other ways (e.g., plasmas for thermonuclear study). Therefore, initially disappointing results were abandoned and not investigated further by the researchers involved to establish the reasons for failure. The analysis revealed that both of the above faults can be readily overcome through proper design and operation, so that there is now no known reason barring at least partial realization of the

early promise of the plasma betatron. Interest in the plasma betatron has led to the analytical study of several features of the device, in particular orbital stability, the efficiency of capture of electrons into accelerating orbits, various beam loss mechanisms, and the economics of the plasma betatron. The findings have been embodied in two publications, *Stability of Orbits in Combined Betatron and Azimuthal Magnetic Fields* and *On the Beam Disruption in a Plasma Betatron*, and a report embodying the present state of knowledge, *Plasma Betatron Study*.

One of the interesting theoretical findings is that the imposition of a toroidal magnetic field has the effect of enabling stable motion in a rather unusual way. Without the toroidal magnetic field, as is already known, motion can be stable at the minimum in the magnetic vector potential which gives rise to the betatron field. This potential plays the part of an effective potential energy for the motion. With the toroidal field imposed, it is found that stable orbits are also possible under certain conditions at radii corresponding to relative maxima in the betatron field magnetic vector potential, which is completely contrary to what one might expect. Among some practical results of the study, of significance for practical industrial application, is that the capital cost per kilowatt of irradiation power output is significantly lower than present accelerators used for the purpose – in fact $< \$10,000/\text{kW}$ of output power. An experimental plasma betatron has been designed, and although only about 40 cm in diameter, it is expected to be capable of pulsed outputs of about 8 MeV and 400 A of electrons.

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TIME-DEPENDENT TRANSPORT CALCULATIONS

The basic idea of this scheme is to solve time-dependent transport problems by considering directly the movement of representative points in a phase space representing the system under study. The usual methods for transport calculations attempt to solve what in general are coupled integro-partial differential equations representing conservation laws applied in the case of the motion of points in phase space. The present scheme instead considers the motion of the points directly, and the conservation laws manifest themselves as a book-keeping procedure for which the computer is ideally suited. This is more in keeping with the capabilities of the digital computer than is the solution of integro-differential equations that the

computer can handle only by going through what are essentially cumbersome and time-consuming procedures. Thus it is not surprising that programs written according to this new method have generated far more detail, particularly as regards the temporal evolution of the systems under study, while using far less computing time, than older methods that depend upon solving the transport equation according to some approximation scheme.

Until recently, work was done with only a single energy group and isotropic scattering. This has now been broadened by the introduction of many groups and nonisotropic scattering. This will enable extension of the technique to more realistic neutron cases, but also ultimately to chemical reactions, slowing down of hot atoms, and to charged-particle problems. Another development in this past year has been the introduction of a phase space which has as its coordinates v versus $x - vt$, instead of v versus x , where v represents velocity, x the distance, and t the time. In this representation the elements of area in phase space do not distort as time evolves. The evolution of the system as increments of time accumulate is easier to follow in such a phase space, whereas previously a complicated algebraic procedure had to be gone through at the end of each time increment to reappportion points before the next increment. To apply the $(v, x - vt)$ phase space, the system is followed in that space until the end of the time span of interest, whereupon the density in the $(v, x - vt)$ phase space is translated back to the usual (v, x) space. So far, work with the $(v, x - vt)$ space has been confined to infinite media, as it has not been decided how to handle boundaries in this scheme.

The (v, x) phase space has been applied to several new problems of interest (e.g., neutron waves, approach to criticality, normal modes, etc.). In particular, it can illustrate the development of normal modes and the calculation of criticality in a thin slab (Figures 23a,b). The vertical lines mark the boundary positions, with vacuum on either side. The vertical scale represents the logarithm of neutron density and the horizontal scale, distance. In both cases, the initial distribution was a uniform density within the slab, zero density outside. Without fission (Figure 21a) it can be seen that the initial uniform distribution decays preferentially at the boundaries until a normal mode is formed, which then continues to decay but maintains its shape as neutrons continue to leak through the boundaries and are absorbed within the media.

Figure 23. Time-dependent transport calculation.

Neutrons escaping to the vacuum regions continue to free-stream out to infinity. In the case of the slab with fission, absorption, and scattering (Figure 21b), the fission ratio has been adjusted so that the normal mode that gets established is stable with time, i.e., criticality. M. ZUCKER, M. TAVEL

ELECTRON RECOMBINATION AFTER PULSED RADIOLYSIS OF GASES AT HIGHER THAN USUAL PRESSURES

The only published data on recombination in gases have been those for relatively low pressures, with the pressure being of the order of about 10 torr or so at the highest. However, it is apparent that many modern scientific, technological, and industrial applications require data at higher pressures (e.g., 100 to 1000 torr). The two difficulties in extending previous methods to the higher pressures has been the impossibility, with existing techniques, of creating a uniform ionization in a well defined region, and of eliminating the effects of the measuring electrodes interacting with the ions and electrons in the medium.

The present method, originally developed in connection with an MHD project, overcomes the first difficulty by using a collimated beam of high-energy electrons from a Van de Graaff accelerator to create the ionization, and the second, by using microwaves as a diagnostic tool. While microwaves have been used before for plasma diagnostics, it is believed that the present combination of an accelerator with microwaves is unique.

Figure 24. Electron recombination after pulsed radiolysis in gases at higher than usual pressures.

The principle of the method is to put the gas being studied into a cylindrical microwave cavity and allow a pulsed collimated electron beam to pass through the cavity along the axis. The ionization causes the resonant frequency of the cavity to change in a way that can be calculated as a function of the instantaneous electron density for the precisely known cavity and column of ionization dimensions. Thus, by following the cavity resonant frequency as a function of time after the electron pulse from the accelerator has passed through the cavity, one can measure the electron density as a function of time. To date, the method has been used for the gases Ar, He, and N₂ at pressures of the order of 1 atm, where recombination coefficients for these gases have heretofore been non-

existent. Typical results are shown in Figures 24a,b. Theory indicates that if $dn/dt = -\alpha n^2$ (where n is the electron concentration and α is the recombination coefficient), the reciprocal of the change of the resonant frequency should vary linearly with time, e.g., Figure 24a. The slope of this curve is simply related to the recombination coefficient, the proportionality constant being exactly calculable from the geometry and the cavity microwave mode of excitation. In Figure 24b the recombination coefficient measured at various pressures of Ar is plotted against the pressure. The results are consistent with the recombination coefficient varying inversely with pressure – as expected on general theoretical grounds. M. ZUCKER, L. FERRARI

BALL LIGHTNING

In the course of work on long-lived metastable electronically excited molecular states for MHD applications, it was realized that the experimental electrical discharges being used were very similar to the reported characteristics of natural ball lightning, and these discharges have been examined to discover their structure.

The work on ball lightning reported previously has been extended to include spectrophotometric measurements of the spectral radiance of the decaying luminosities as a function of time for air, N_2 , O_2 , and N_2-O_2 mixtures with CO_2 and H_2O . The radiance varies with wavelength, but averages about $0.10 \text{ W/cm}^2 \text{ sr } \mu$ at wavelengths between 0.3 and 1.3μ . Very strong OH peaks (0.3064μ) are seen, with a radiance $>1 \text{ W/cm}^2 \text{ sr } \mu$. Considerable structure is seen in the spectrum; with identification from simultaneous spectrographs, it should be possible to derive excited species concentrations and reaction rates.

A simplified analytical model for ball lightning was developed that predicts a stable ball-like discharge. If a ball is formed as part of a lightning stroke channel, or by field emission from structures, Townsend discharge in the ball due to the pervading atmospheric dc field can maintain it, at fields comparable to those found in nature.

The re-forming reaction takes place at 900°C in a fluidized coal bed, heated by heat exchange with the MHD exhaust. A study of the re-former showed practical reaction rates and a high degree of conversion. The main technical problem is strength of materials at these elevated temperatures, but this appears solvable.

Approximately 38% of the input energy to the coal-nuclear cycle is nuclear; the balance is coal. In the range of \$0.21 to \$0.27 per million Btu for coal, this hybrid cycle had lower power costs than either separate coal or nuclear.

A wide range of operating parameters was investigated to find optimum cycle conditions. This included studies of the effect of combustion pressure, diluent/combustion ratio, and preheat temperature. Pressures of 30 atm, diluent ratios of 1/1, and preheat temperatures of 900°C were found to be attainable and efficient. In addition, two new effects are predicted, a positive ion space-charge limited current from the ball, which can collect negative current from an area much larger than the ball, and an electrohydrodynamic force from this current that tends to stabilize the ball against convective mixing and can explain its puzzling motion, where it sometimes goes through small openings, or against the wind. A numerical one-dimensional computer solution was obtained, showing a stable discharge. A three-dimensional solution is now being written.

J. POWELL,
R. DOMISH

EQUILIBRIUM MHD CYCLES WITH FOSSIL-FUEL, NUCLEAR ENERGY INPUT

A new MHD cycle that uses a combination of fossil fuel and nuclear energy input was investigated (see Figure 25). Coal or methane gas is reformed to hydrogen using nuclear generated steam (in a PWR or BWR). The endothermic heat of reaction is obtained from the sensible heat of the MHD exhaust (exit temperature, $\approx 2000^\circ\text{K}$). The scrubbed hydrogen is then burned with oxygen from an air separation plant, diluted with either steam or an inert gas, and sent through an MHD generator.

There are a number of significant advantages to this cycle.

1. High efficiency, 55 to 60%.
2. Clean fuel for MHD (no ash).
3. Condensing cycle, no compressors required.
4. Easy cesium seed recovery.
5. Low preheat temperatures with high efficiency. The chemical fuel transformation is equivalent to very high preheat temperatures.
6. More than 90% of the output power would come from the MHD generator.
7. No pollutants (such as ash, SO_2 , or NO) released to the atmosphere.

Figure 25. Fossil-nuclear fueled MHD power cycle. H₂-O₂ system.

The preliminary evaluation indicates that the system allows fossil fuel to compete with nuclear energy in high fossil fuel cost areas and conversely, it allows nuclear energy to compete in low fossil fuel cost areas, thus expanding the market for both fuel sources. Further detailed investigation of the system is recommended. M. STEINBERG, J. POWELL, M. BELLER, H. KATZ

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Hot Laboratory Division

L.G. STANG JR.

Nuclear and Radiochemical Research on Special Isotopes

M. HILLMAN

SZILARD-CHALMERS REACTIONS

The behavior of zirconium and hafnium atoms during and following irradiation of the organic compounds zirconocene and hafnocene is of interest because of the information concerning nuclear energy levels and atomic bond strengths that can be deduced from it. The effects studied include the amount of primary retention (i.e., the fraction of activated metal atoms that never leaves the parent molecule), the amount of recoil (i.e., the fraction of induced activity that permanently leaves the original molecule), and the apparent retention (i.e., the activated atoms that recoil out and recombine with the same or similar molecule).

In a study of these effects, experiments in which the specific activity of irradiated zirconocene remained constant demonstrated that little, if any, decomposition of zirconocene dichloride occurs during evaporation and sublimation. However, it was noted that decomposition did occur in the following instances: when hafnocene (but not zirconocene) was dissolved in 10% dimethyl sulfoxide (DMSO)-90% benzene, when zirconocene (and, of course, hafnocene) was dissolved in 50% DMSO-benzene, and when zirconocene dissolved in 10% DMSO-90% benzene was briefly irradiated with thermal neutrons. This difference in chemical behavior between similar zirconium and hafnium compounds in these solutions is remarkable and deserves further investigation.

Although retentions during irradiation of solutions often depend on the polarity of the solvent used, experiments with mixtures of benzene and acetone, in the anhydrous as well as moist states, indicated no effect of solvent polarity on hafnium retention and virtually none on that of zirconium, while the presence of water in the solvents reduces both retentions slightly.

Thermal neutrons, which produce (n, γ) reactions, and 14-MeV neutrons, which produce (n, n') and $(n, 2n)$ reactions, were both used to irradiate the hafnium and zirconium compounds. The retentions observed in the 14-MeV neutron experiments are in the same range as those observed for the 14-MeV neutron experiments with the phthalocyanines of these two metals. However, we had previously noted a very surprising isotope effect, not expected under these conditions. Since the recoil energy imparted by the capture of the 14-MeV neutrons is sufficient to break all bonds and to remove the recoiling atom far from its source, all of this retention (when 14-MeV neutrons are used) must be due to displacement reactions.

In the study of the phthalocyanines the same series of experiments had revealed that, within experimental error, the retentions from 14-MeV neutron experiments plus the retentions from (n, γ) experiments in solution were equal to the retentions from (n, γ) experiments carried out in the solid state. This was easily explained, since retentions from the (n, γ) experiments in the solid state were due to a combination of effects: processes in which no bonds were broken, those in which bonds were broken but quickly re-formed, and processes in which bonds broke and the recoiling atom displaced a chemically similar atom in another molecule. Only the first two can take place in solution with any reasonable probability, and only the third can take place following 14-MeV neutron reactions; this, then, explains the additive property to give the retentions of (n, γ) reactions in the solid state. However, *if* (perhaps for some chemical reason) bonds cannot be re-formed, once they are broken, the additive property will not hold. This appears to be the case with metallocenes. Retentions in solution may still involve some recombination, but a large part of it apparently does not occur.

The explanation may lie partly in the fact that the metallocene molecule has no existence independent of the metal, whereas the phthalocyanine

molecule does exist independently even in the absence of a metal atom, thereby providing a far greater possibility for recombination in the latter system.

In an experiment to determine the extent of possible diffusive recombination, a sample of hafnocene dichloride irradiated by thermal neutrons was heated to 100°C and then sublimed directly without any intervening chemical purification. The results indicated that there had been no annealing and therefore no diffusive retention.

The various retentions observed are summarized in Table 1. The $10.1 \pm 0.2\%$ and $11.4 \pm 0.8\%$ retentions found for the $(n,2n)$ reactions leading to Zr^{89} and Zr^{95} , respectively, in solid zirconocene agree closely with the $9.92 \pm 0.49\%$ and $11.1 \pm 0.10\%$ retentions found for Hf^{180m} and Zr^{89} following (n,n') and $(n,2n)$ reactions, respectively, in solid hafnocene, but differ considerably from the $1.70 \pm 0.18\%$ and $3.77 \pm 0.35\%$ retentions following $(n,2n)$ reactions forming Hf^{173} and Hf^{175} , respectively. They also differ from the $\approx 3\%$ retention observed in the $(n,2n)$ reaction forming Zr^{89} in zirconium phthalocyanine.

This isotope effect is apparently real, for it was verified in repeated experiments on hafnocene, although it was not found in zirconocene. It was certainly unexpected because since all bonds are

broken by 14-MeV neutron capture and since we would therefore expect all of the retention to be due to displacement, it should be the same for all nuclides. A suggested explanation involves the production of unknown isomers of these nuclides which decay and recoil, reducing the retention.

A. WEISS, M. HILLMAN

RECOIL FROM THE $Ca^{48}(\alpha,an)Ca^{47}$ REACTION

The high yields from (α,an) reactions in neutron rich targets continue to be of interest. Of particular interest are the observed high yields for the $Ca^{48}(\alpha,an)Ca^{47}$ reaction [B. GORDON, The interaction of calcium-48 with 17- to 39-MeV alpha particles. *Nucl. Phys. A98*, 403-8 (1967)] on the low energy side of the excitation function. Information about the mechanism of this reaction can be obtained by observing the Ca^{47} recoil range, which is a measure of the momentum transferred to the target nucleus during the reaction (e.g., compound nucleus formation would transfer all momentum and give a maximum recoil range, while an indirect mechanism would transfer only part of the momentum and give a shorter recoil range).

Such experiments require thin foils. Apparently successful foils of a calcium basic nitrate on quarter-mil Mylar on which a very thin film of alumi-

Table 1

Retention of Zr and Hf in Metalloenes

Composition of sample	Hf ^{180m}	Hf ¹⁸¹	Hf ¹⁷³	Hf ¹⁷⁵	Zr ⁸⁹	Zr ⁹⁷	Zr ⁹⁵
Zirconocene and hafnocene							
Solid							
(n,γ)	0.597± 0.033	0.207± 0.017		0.171± 0.024		0.150± 0.004	0.213± 0.016
Hafnocene							
Solid							
(14 MeV n)	0.0992± 0.0049 (n,n')		0.0170± 0.0018 (n,2n)	0.0377± 0.0035 (n,2n)	0.111± 0.010 (n,2n)		
Zirconocene							
Solid							
(14 MeV n)					0.102± 0.002 (n,2n)		0.109± 0.013 (n,2n)
Zirconocene and hafnocene in benzene (n,γ)	0.225±	0.0537±				0.0104±	0.0221±
Wet	0.006	0.0021				0.0005	0.0030
Zirconocene and hafnocene in benzene (n,γ)	0.256±	0.0582±				0.0139±	0.0339±
Dry	0.012	0.0034				0.0012	0.0030
Zirconocene and hafnocene in 50% mixture of benzene and acetone (n,γ)	0.224±	0.0534±				0.0073±	0.0179±
Wet	0.011	0.0010				0.00014	0.0013
Zirconocene and hafnocene in 50% mixture of benzene and acetone (n,γ)	0.257±	0.0608±				0.00829±	0.0214±
Dry	0.029	0.0041				0.00053	0.0047

num had been vacuum deposited were prepared by a molecular plating technique [W. PARKER, H. BILDSTEIN, AND N. GETOFF, Molecular plating. I. A rapid and quantitative method for the electrodeposition of thorium and uranium. *Nucl. Instr. Methods* 26, 55 (1964)]. The calcium deposits were a few thousand angstroms thick and were not disturbed by rubbing a finger lightly across the foil; they are stable to air and moisture. B. GORDON

CHEMICAL EFFECTS OF RADIOACTIVE DECAY

A study was begun of the chemical effects accompanying the decay of Xe^{125} to I^{125} :

Specifically the distribution of oxidation states of iodine resulting from reactions of excited iodine atoms in high charge states will be determined. These high charge states are due to the Auger effect after the electron capture process in the parent Xe^{125} .

In a previous study [B.M. GORDON, A study of the chemical effects of β decay from Te^{132} to I^{132} using paper electrophoresis. *J. Inorg. Nucl. Chem.* 29, 287-91 (1967)] of the distribution of iodine oxidation states resulting from the decay of Te^{132} to I^{132} , the I^{132} was also produced in a highly charged state because of the internal conversion process following beta decay. In that case the "hot" iodine atom was incorporated in a particular molecular species, and the distribution of iodine oxidation states was observed as a function of the molecular species containing the parent tellurium. The present experiment, in which the parent Xe^{125} is a free atom, will show the reactions of a hot iodine atom with the solvent without the complication of it being part of a larger species, which would use up energy in breaking bonds.

Work thus far has been concerned with the separation of iodine oxidation states. Electrophoresis, applied in the earlier tellurium-iodine study, is unsuitable here because of the amount of the activity that can be analyzed. A Dowex-1 anion exchange procedure was tried briefly and dropped when periodate was found to be reduced on the column. Meanwhile a scheme has been worked out involving extraction of elemental iodine into CCl_4 and precipitation of tetraphenylarsonium periodate. B. GORDON

EPITHERMAL NEUTRON PRODUCTION OF TRANSPLUTONIC NUCLIDES

The possible superiority* of epithermal neutrons over thermal neutrons for producing transplutonic nuclides is being studied. A Cf^{252} sample,** shielded with 60 mils of cadmium, was irradiated for 20 days in the HFBR in an epithermal flux per unit lethargy of $\approx 7 \times 10^3 \text{ n-cm}^{-2}\text{-sec}^{-1}$. The neutron activities of the irradiated sample and of a similar but unirradiated sample used as a control were determined with six BF_3 counters. Most of the effort on this problem involved trying to explain the results, shown in Figure 1. This figure shows the ratio of the neutron activity of the irradiated sample to that of the unirradiated portion of Cf^{252} , both sources from the same origin; the vertical bars are the statistical standard deviations. (A horizontal line would mean that no change in isotopic composition had occurred during irradiation.) The two reference curves, labeled 1% and 5%, represent neutron activity ratios that should have been observed if the Cf^{254} in the sample at the time of the first count were 1% or 5%, respectively.

The major observations are the apparent absence ($< 1\%$) of Cf^{254} and the increase of Cf^{252} in the sample, presumably due to production from Cf^{250} and Cf^{251} present in the sample. Undoubtedly the initial decay and growth following irradiation is not real, and the curve probably should be horizontal, indicating little, if any, change in the isotopic composition, although an observed growth of Cf^{252} could indicate the existence of an isomeric state that decays to Cf^{252g} .

If all of Prince's cross section estimates (*op. cit.*) for processes involving fission and capture for Cf^{252} , Cf^{253} , and Cf^{254} were correct, we should have observed an 85% increase in the neutron activity (representing production of 0.2 atom % Cf^{254} and 25% burnup of Cf^{252}). Additional subsequent counting of the tail of the curve, measurement of the dead-time of the counter, and a least-squares computer analysis of the data indicated that the Cf^{254} neutron activity is $0.2 \pm 0.1\%$ of the total neutron activity, which is equivalent to 4.1×10^{-4} atom %. Because of the many degrees of freedom associated with the number of unknown cross sec-

*First suggested by W.E. Winsche (private communication) and subsequently predicted by A. Prince (Thermal neutron cross sections and resonance integrals for transuranium isotopes, BNL memorandum to S. Pearlstein, January 12, 1967).

**The actual composition was: 70% Cf^{252} , 1 to 2% Cf^{251} , 5 to 20% Cf^{250} , 5 to 12% Cf^{249} , 0.1% Es^{254} , and $< 5\%$ Cm^{244} .

tions and the limited experimental observations, many reasonable combinations of estimated isotopic abundances in the sample and capture cross sections yield results that agree with what was observed. However, all cases seem to require a capture resonance integral for Cf^{251} that is many times Prince's estimate of 172 b and an absorption cross section for Cf^{252} that is many times lower than the predicted 970 b.

Folger et al. (R.L. FOLGER, J.A. SMITH, L.C. BROWN, R.F. OVERMAN, AND H.P. HOLCOMB, Foil measurements of integral cross sections of higher mass actinides. Conf. Neutron Cross Sections and Technol., Natl. Bur. Std. (U.S.), Washington, D.C., March 4-7, 1968) recently reported measurements of the capture resonance integral for a number of nuclides including Cf^{250} , Cf^{251} , Cf^{252} , and Es^{253} . By using their experimental results and more critical treatment of our data, we were able to establish a value of 21 ± 11 b for the capture resonance integral for Cf^{253} and to corroborate the cross sections that they report. Figure 2 (solid line) shows the relationship between the initial

abundances of Cf^{250} and Cf^{251} needed to yield the observed increase of Cf^{252} , assuming Folger's reported resonance capture integrals of 5300 b for Cf^{250} and 980 b for Cf^{251} . The hatched area of the figure represents the reported ranges for the initial abundances in the californium samples, and the proximity of the line to the hatched area indicates the consistency of our results with the cross sections reported by Folger.

Because of the obvious difficulties in interpreting the results of the kind of experiment described above owing to the many degrees of freedom involved, a systematic determination of individual cross sections was begun concurrently. The procedure involves the deposition of known amounts of target material on mica, which is then irradiated and subsequently etched with concentrated hydrofluoric acid to reveal the fission tracks, which are then counted under an optical microscope. Inasmuch as the thickness of the targets must be small relative to the range of fission products, we have successfully used the molecular plating technique (W. PARKER et al., *op. cit.*) to make some uranyl nitrate deposits that are quite uniform and only a few thousand angstroms thick.

B. GORDON, E. WEINSTOCK

Figure 1. Decay of ratio of neutron activities in the irradiated 0.1- μg Cf^{252} source and an unirradiated 0.1- μg Cf^{252} standard source.

Figure 2. Relationship between starting abundances consistent with Cf^{252} increase. Hatched area represents estimated range of starting abundances.

TERNARY FISSION

A three-parameter triple-coincidence apparatus continued to be used to record energies of ternary fission fragments emitted when thermal neutrons bombarded the following targets: U^{233} , U^{235} , Pu^{239} , and Pu^{241} . The data, collected until the Brookhaven Graphite Research Reactor was shut down in June 1968, were very reproducible for different targets of the same nuclide; they also showed characteristic differences for targets of different nuclides. Neutrons in triple coincidence were measured at various angles including 120-120-120° and 130-100-130°. Moreover, thin (0.52 mg/cm²) aluminum absorber foils placed in front of each of the three detectors and energy thresholds used on the three multichannel analyzers insure that only ternary fission fragments and not recoiling target nuclei will be registered. The results obtained are consistent with the interpretation that triple events registered at the 120-120-120° angular positions are predominantly ternary fission events rather than scattering events and support the dominant role of underlying shell structure in determining the three-way nuclear cleavage.

In a different attack on the same problem, a radiochemical search was made in an effort to detect the chain

in an aged irradiated U^{235} fuel plate sample that contained 10^{19} fission events. The interest in this stems from the unaccountably large amount of Si^{32} that had been observed in fallout and because earlier work on ternary fission had indicated a light fission fragment peak at mass 30 to 32. The isolation procedure consisted of dissolving the sample and carrier in dilute HNO_3 containing Ag^+ ions and oxidation by MnO_4^- at elevated temperatures, followed by standard separation and purification routines. Chemical yields were satisfactory (20%) and radiochemical purity of the P^{32} (as PO_4^{3-}) was high. As a result of this work an upper limit for the yield of Si^{32} can be set at 10^{-10} atoms per fission of U^{235} .

The increased mass-energy conversion for ternary fission relative to binary fission and the decreased total kinetic energy measured for the fragments indicate a larger amount of excitation energy (initially present as deformation energy) in the

Figure 3. Cadmium-loaded liquid scintillator with centrally located ternary fission chamber (not shown). Experimental assembly for detection of neutrons associated with ternary fission of Cf^{252} . A triple coincidence in the fission chamber announces the occurrence of a ternary fission event. A coincident pulse (due to proton recoils from fast neutrons and prompt fission gamma rays) is required to open a gate for 30 μ sec and for triggering the sweep signal of an oscilloscope. The neutrons from the fission event are slowed down in the liquid scintillator and eventually captured (mean time of 10 μ sec) by Cd^{113} releasing a cascade of gammas from the (n,γ) reaction. Each capture process results in a large scintillation output that is recorded by the scaler and that appears also as a spike on the oscilloscope face and finally on photographic film. Simultaneously, the three energies of the ternary fission event are recorded in the usual manner by the three-parameter analyzer.

resulting three fragments. This excessive energy must be removed by neutron evaporation and gamma-ray emission. Hence, for ternary fission one would expect an increased value of $\bar{\nu}$, the average number of neutrons emitted per fission. Observation of such an increase would confirm the existence of ternary fission. Moreover, a knowledge of $P(n)$, the probability of emitting n neutrons in the ternary fission process, would be useful in developing a mechanism for the process.

To measure these parameters, a neutron detector was constructed (Figure 3) comprising a 100-liter gadolinium-loaded liquid scintillator viewed by thirteen 5-in. photomultiplier tubes. Into the center of this detector was placed the ternary fission detector chamber used on the studies described above, and in the center of the ternary fission de-

tector was located a Cf^{252} source that is spontaneously fissioning at the rate of 10^5 dis/min. The arrangement, which has just now been assembled and tested, is expected to register several triple coincidence events per week. M. MUGA, M. HILLMAN

NUCLEAR LEVEL DENSITIES

The ability to compute, and hence predict, the closeness of the spacing between energy states in excited nuclei, i.e., their level densities, is important for the fundamental understanding of nuclear structure and the practical prediction of the direction and yields of complicated nuclear reactions. In such a computation one parameter that is difficult to evaluate is the pairing correction, i.e., the energy contributed to the entire nucleus by the pairing of two nucleons.

Several attempts have been made at pairing corrections through the use of a degenerate formula that would make the computed level densities agree with the measured level densities, where measured data are available. The fits thus obtained were not particularly good. Therefore, the

rigorous BCS pairing formulation was used [P.A. SEEGER, A model-based mass law, and the r . process as a mass law test. LA-3571; S. WAHLBORN, Effects of blocking on the level spacings of odd-mass deformed nuclei. *Nucl. Phys.* **37**, 554 (1962)].

In solving the BCS equations a mathematical difficulty arises in that a real value of the pairing parameter Δ is not always obtainable. From trends in the value of Δ^2 with various configurations we found that assignment of $\Delta^2=0$ for unsolvable cases involves introduction of only small errors.

The level densities of five nuclides surrounding the closed 50-proton shell, each containing 66 neutrons, were determined. From this work we can call attention to two properties (Figure 4): (a) there appears to be an energy gap for In, Sn, and Sb, and (b) there appear to be waves with ≈ 4.5 -MeV wavelengths on all curves except that of Te. Both effects are clearly associated with the 50-proton closed shell and are explained simply as follows: Very few levels can be observed with no nucleons above the 50-proton shell or with only one above and the 50-proton shell filled. However, as soon as a proton is promoted above this shell, a large number of levels become available from complex configurations. At higher energies, without further promotion, the increase in the number of levels becomes less, and finally with further promotion at still higher energies the rate of increase of numbers of levels again increases. The wavelength should then be associated with the energy gap immediately above the 50-proton shell, which is ≈ 4 MeV.

The level densities (log scale) of Cd^{114} and Ho^{166} are shown in Figures 5 and 6, respectively, plotted against the energy E and spin J . The plots are best visualized as a promontory viewed at a 45° angle by someone standing on the E, J plane. The height of the promontory at any point is the logarithm of the level density. The smooth curves are at constant energy (0.5 MeV apart for Cd^{114} , 0.3 MeV apart for Ho^{166} , with energy increasing as one goes up the promontory and J increasing from left to right); the zig-zag curves connect points at constant J . Note the wave structure clearly evident for Cd^{114} and persisting at all J 's. Note also the varying curvatures of the constant E curves. This is evidence for differing moments of inertia at differing energies.

Concerning the question "Are the level densities for positive parity the same as for negative parity?", this work has shown that this is close to being true

Figure 4. Level densities of five 66-neutron nuclides surrounding the closed 50-proton shell.

Figure 5. Log level density, W , plotted against energy, E (increasing to the rear) and spin, J (increasing to the right) for $^{48}\text{Cd}^{114}$.

Figure 6. Log level density, W , plotted against energy, E (increasing to the rear) and spin, J (increasing to the right) for $^{67}\text{Ho}^{166}$.

but that there are notable exceptions when the ratio of numbers of single-particle levels for one parity relative to the other exceeds eight.

Two apparent anomalies in neutron resonances had been noted in two pairs of nuclides, $\text{Fe}^{55,57}$ and $\text{Ni}^{59,61}$, wherein the members of each pair differing by only two neutrons had the same level densities at the neutron resonance energies, despite the fact that the resonance energies differ by 1 to 1.5 MeV. However, after systematic examination of one of the parameters in the BCS formulation,

we found that the agreement between the measured and calculated level densities is quite reasonable and that there is no anomaly. M. HILLMAN, J. GROVER*

NUCLEAR EVAPORATION CALCULATIONS

The previous study of nuclear evaporation processes [J.R. GROVER AND J. GILAT, De-excitation of highly excited nuclei. *Phys. Rev.* 157, 802 (1967)] was resumed in order to obtain further insight into the processes that govern the de-excitation of highly excited nuclei at high angular momenta. This work is being extended into regions of the periodic table in which charged particle (rather than merely alpha particle) emission is expected to play an important role.

Preliminary results indicate that in tellurium compound systems ($A \leq 118$), alpha particle emission dominates the de-excitation process, especially at high angular momenta, but proton evaporation is the dominant mode in bromine compound systems below $A = 74$. One conclusion implied by these results is that the limits on the production cross section of highly neutron deficient nuclides, imposed by the increasing difficulty of neutron evaporation, vary greatly between different regions of the periodic table, and even between adjacent nuclides. Also, some nuclides may be produced more efficiently in low angular momentum systems (proton-induced spallation) than in high angular momentum (heavy-ion-induced compound nucleus) reactions. J. GILAT, J. GROVER*

Analytical Chemistry Research

L. NEWMAN

MIXED-METAL COMPLEXES

The behavior of indium and other metals with certain organic acids continues to be studied in order to determine the structural requirements and other necessary conditions for forming mixed-metal complexes and the stability of the complexes formed. For example, the addition of chromium causes a tenfold decrease in the extraction of indium by thenoyltrifluoroacetone (TTA) in the presence of itamalic acid. Added aluminum in-

*Member of the Chemistry Department.

creases eightfold the extraction of indium by TTA from a citrate-acetate system, although in the absence of indium TTA was found not to extract aluminum from citrate. On the other hand, cerium causes no noticeable change in the indium distribution coefficient in the same citrate system. Also, the presence of acetate (used to buffer the pH to 4) was found not to affect the distribution of indium. In order to facilitate attainment of equilibrium when chromium(III) was a constituent (for chromium is known to attain equilibrium slowly), experiments were done at 45°C, but separate experiments verified the fact that the mixed-metal complexes are formed equally well at room temperature and are not dependent on elevated temperatures. Still other experiments showed that under the conditions studied, equilibrium was indeed reached well within the time limit allowed. Equilibrium was also shown not to depend on indium concentration.

The three metals that have been found to hinder the TTA extraction of indium are readily hydrolyzed, suggesting that hydroxy bridging might be involved in the formation of the mixed-metal complex. However, when thallium(III), which is strongly hydrolyzed, was substituted for chromium(III) under otherwise identical conditions, no inhibitory effect on the TTA extraction of indium was observed, indicating that hydroxy bridging is probably not involved in the mixed-metal complex.

To determine whether only hydroxy acids are capable of forming this type of mixed-metal complex, aspartic acid was used in place of malic acid in a solvent extraction involving Cr(III) and In(III). The structures of the two acids are identical except aspartic acid has a NH_2 — group in place of an OH — group. Malic acid had been found to form a mixed-metal complex, but aspartic acid did not, suggesting but not proving that the hydroxy group is needed in the complex.

With the use of the same techniques, we showed that the UO_2^{+2} ion forms an even stronger mixed-metal complex with indium(III) and citrate than chromium(III) does, a minimum value of the equilibrium constant being $\approx 10^7$ at pH 4. However, when dicrotalic acid (which does not form a mixed-metal complex with chromium and indium) was substituted for citric acid, it still failed to form a mixed-metal complex with UO_2^{+2} and In(III).

Titration experiments, which took advantage of the strong complex formation of the UO_2^{+2} ion,

showed that in forming the $\text{UO}_2^{+2}/\text{Ce}^{+3}$ /citrate complex four protons were liberated per molecule of citric acid; this corresponds to all of the displaceable protons on the ligand and differs from the corresponding case in the absence of Ce(III) , in which case only three protons per molecule of citric acid are liberated. Also in the case of the $\text{UO}_2^{+2}/\text{In}^{+3}$ /citrate complex four protons per molecule of citric acid are liberated.

Spectrophotometric experiments showed that the $\text{UO}_2^{+2}/\text{In}^{+3}$ /citrate complex contains a molecular ratio of 1:1:2, and other titration experiments indicated clearly that a single complex rather than a mixture of UO_2^{+2} /citrate and In^{+3} /citrate complexes was involved. The formation constant was calculated to be 4.1×10^5 . The fact that this is greater than the dimerization constant (1.2×10^4 liter-moles $^{-1}$ at 25°C) of uranyl citrate in 1 M KNO_3 shows the importance of both mixed-metal complex formation and the concentrations of the individual metal ions in devising an analytical technique involving extraction from aqueous citrate media.

Other experiments were performed in which the degree of polymerization of the various ions was measured under various conditions. As a result, it should be noted that in an aqueous solution containing metal ions M_1 and M_2 with an excess of ligand L (where L = malate or citrate), the following equilibria must be considered:

L. NEWMAN, A. ADIN, P. KLOTZ, T. GILBERT*

DIMERIZATION OF SUBSTITUTED TRIPHENYLAMINE CATION RADICALS

Recent studies of the electrochemical oxidation of substituted triphenylamines (TPA) have indicated that the cation radical undergoes dimerization to give the corresponding tetraphenylbenzidine (TPB). Marcoux, Adams, and Feldberg [L.S. MARCOUX, R.N. ADAMS, AND S.W. FELDBERG, Dimerization of triphenyl cation radicals. (In

*On leave from the U. of Cincinnati.

preparation.)) evaluated the rate constants of dimerization for several of these substituted triphenylamines from experiments with the rotating disc electrode. More recently chronoamperometry was used to study the rate of dimerization of several substituted triphenylamine cations. The rates ranged from 9.4×10^1 liter-moles⁻¹-sec⁻¹ for 4-methyl TPA to 6.8×10^3 for the 4-nitro TPA.

Recently the rotating disc electrode was shown to be feasible for evaluating the kinetics of a first-order ECE reaction mechanism [P. MALACHESKY, L.S. MARCOUX, AND R.N. ADAMS, Homogeneous chemical kinetics with the rotating disc. *J. Phys. Chem.* **70**, 4068 (1966)]:

$A \xrightleftharpoons{e^-} B$ Electron transfer

$B \xrightarrow{k} C$ Chemical step

$C \xrightleftharpoons{e^-} D$ Electron transfer

The validity of their approach is limited, as was shown by Karp's more rigorous calculations and in our paper on this subject (*op. cit.*).

These calculational limitations, as well as our interest in a variety of ECE type mechanisms, led us to develop a method of digital simulation of the hydrodynamic-diffusion-kinetic processes at the rotating disc electrode. A simple modification of a previously described digital simulation technique treats the hydrodynamic aspects of the problem. A complete description of this digital simulation technique is presented elsewhere [S.W. FELDBERG, Digital simulation: A general method for solving electrochemical diffusion-kinetic problems. *Advan. Electroanal. Chem.* **3** (in press)].

In our paper the effects of introducing various kinetic complications into the basic rotating disc electrode calculation are presented, and the second-order rate constants for the dimerization of several substituted triphenylamine cations are evaluated.

S. FELDBERG

Figure 7. Special target assembly for Van de Graaff accelerated triton beam irradiation of Mg^{26} .

Medical Radionuclides

P. RICHARDS

MAGNESIUM-28

Interest in magnesium-28 as a tracer in medical and biological research has increased because the magnesium cation is thought to control several important processes including cell permeability, neuromuscular function, enzyme activation, and protein synthesis, and because magnesium-28 is the only possible radiotracer for magnesium. Since 1955 magnesium-28 has been produced at Brookhaven by reactor irradiation of $\text{Li}^6\text{-Mg}^{26}$ alloy utilizing the $\text{Li}^6(n,t)\text{He}^4$ and $\text{Mg}^{26}(t,p)\text{Mg}^{28}$ reactions. Understandably the specific activity of the product ($20\ \mu\text{Ci Mg}^{28}/\text{g Mg}$) has been low and, for many important studies, barely adequate. Curtailment of the operation of the BGRR stimulated development of a method of making Mg^{28} by bombarding the end of a $1/4$ -in. diam rod of enriched Mg^{26} with 3.4-MeV tritons accelerated by a Van de Graaff generator. The rod is clamped in a water-cooled split chuck, which, in turn, is mounted onto the beam port of the Van de Graaff (Figure 7). Following irradiation, a small Teflon cup with a hole in the bottom is pressed over the rod so that its end is flush with the inside bottom of the cup. Dilute HCl, added to the cup, is used to etch only the first 1 to 2 mils from the end. Inasmuch as $\approx 95\%$ of the activity is expected in the first 1.5 mils, this technique produces high specific activity and permits reuse of the same rod many times. Yields have been $\approx 50\ \mu\text{Ci Mg}^{28}/\mu\text{Ah}$, very close to expected values, and specific activities of $>200\ \text{mCi Mg}^{28}/\text{g Mg}$ are achieved routinely. Still higher specific activities are obtainable with longer bombardments. Gamma-ray spectrometry and decay studies indicate a final product of extremely high radiopurity ($<0.001\%$ radiocontamination).

TECHNETIUM -99m

Separation

A solvent extraction procedure [P.V. HARPER, K.A. LATHROP, F. JIMINEZ, R. FINK, AND A. GOTTSCHALK, Technetium-99m as a scanning agent. *Radiology* 85, 101-9 (1965); J.B. GERLIT, Some chemical properties of technetium. In *Proc. UN Int. Conf. on Peaceful Uses of Atomic Energy, Geneva,*

1955, Vol. 7, pp. 145-51, UN, New York, 1956; P. RICHARDS, The technetium-99m generator. In *Proc. Symp. Radioactive Pharmaceuticals, Oak Ridge Institute of Nuclear Studies, Nov. 1965*, CONF 651111.] is currently used at Brookhaven for supplying Tc^{99m} for intra-Laboratory use. The product purity is comparable to that achieved with the regular BNL-developed Tc^{99m} generator but only when the latter is loaded with fission product Mo^{99} (rather than with irradiated stable molybdenum) or when the ion exchange column comprising the generator is inconveniently large. Other advantages of this method include lower cost and the fact that it is the only practical means of supplying Tc^{99m} in situations in which only a relatively low neutron flux is available. However, several difficulties developed in the procedure, and, because of the evident importance of the method, the various steps in the technique were systematically investigated in order to maximize reproducibility, efficiency, and product purity.

The method involves the extraction of Tc^{99m} as pertechnetate ion into methylethyl ketone (MEK) from a strongly basic solution of irradiated MoO_3 . Figure 8 illustrates the simplicity of the equipment used. Traces of contaminating aqueous phase were found to be eliminated by passing the organic phase through sterile absorbent cotton prior to evaporation. Low yields in the residue-dissolving step were corrected by placing in the vessel prior to evaporation of the MEK a weighed amount of NaCl crystals on which the Tc^{99m} deposits directly; solution of the NaCl in sterile water recovers virtually all the Tc^{99m} in a form ready for injection.

Yields of Tc^{99m} across the extraction step were found to be $>99\%$ provided that the NaOH solution is $>2\ N$ and the volume of MEK is $>7\ \text{ml}$ (for 10 ml of aqueous phase). However, a NaOH concentration of $>5\ N$ was found to be needed to prevent Mo^{99} from extracting with the technetium. If too high an evaporation temperature is used, the MEK apparently partially decomposes causing subsequent difficulties when the Tc^{99m} product was used to label organic compounds; use of a lower evaporation temperature corrected the trouble.

Labeling

Gel chromatography was found to be very useful in studying the stability and behavior of labeled compounds and the yields with which human serum albumin, citrate, and DTPA can be labeled

Figure 8. Equipment for extraction of Tc^{99m} from irradiated MoO_3 . All manipulations of the equipment, which is used behind a shielding wall, are performed with a simple pair of wall-mounted tongs. A 5 *N* NaOH solution of irradiated molybdena is transferred to the magnetically stirred beaker to which is added methylethyl ketone. After being stirred for several minutes, the liquids are poured into the separatory funnel, and the aqueous Mo^{99} -containing phase is returned to the bottle for reuse while the MEK is run through the sterile cotton column. The collecting beaker, containing NaCl crystals, is gently heated to dryness on the hot plate under a stream of filtered air or nitrogen. The residue is dissolved in sufficient sterile water to make a physiological saline solution, which, after passage through a sterile Millipore membrane, is ready for use.

with Tc^{99m} . It is also useful in separating pure fractions of the labeled material from reactants and impurities. A convenient small rapidly flowing column can be made from a 30-cc disposable plastic syringe filled with Sephadex G25*. Such columns, maintained in a sterile condition by closing the top with a multiinjection stopper and eluting with saline solution containing benzoyl alcohol, are useful for rapid purification of Tc^{99m} -labeled HSA and DTPA prior to use.

Table 2		
Magnesium-28 Shipped (mCi)		
	1967	1968
Jan	300	250
Feb	600	1400
Mar	700	600
Apr	400	^a
May	350	600
June	800	950 ^b
July	300	^b
Aug	100	500 ^c
Sep	100	—
Oct	250	200 ^c
Nov	50	400 ^c
Dec	750	250 ^c

^aBGRR shutdown caused cancellation of 7 shipments.

^bNote that BGRR shut down permanently on June 10, 1968.

^cVan de Graaff-produced.

TELLURIUM-125_m

Solvent extraction was used several times to separate 60 to 70 mCi of carrier-free Te^{125m} from its parent Sb^{125} , with $<10^{-3}\%$ of the latter remaining as contamination. Although the Te^{125m} will be used for studies of medical applications, two batches were given to the Chemistry Department for studies of the Mössbauer effect and of the effect of chemical environment on decay. A third batch went to the Argonne Cancer Research Hospital for some collaborative studies. Meanwhile a vacuum system was built for determining the feasibility of distilling the tellurium away from its antimony parent and tin grandparent.

Hot Laboratory Operations

P. RICHARDS

ISOTOPE PRODUCTION

In 1967 Brookhaven turned over its isotope production to private industry, retaining only Mg^{28} and miscellaneous items of infrequent demand. Therefore, in 1968, Mg^{28} was the only radioisotope produced for distribution except for six 20-mCi shipments of I^{133} , one of 100 unirradiated yttrium beads, and one of 20 mg of Li^6 - Mg^{26} alloy. This is reflected in Table 2. Note that the demand for Mg^{28} waned in the Spring of 1967 but in-

creased markedly at the end of the year and continued high until production was completely halted by the shutdown of the BGRR. With the development of the Van de Graaff production noted above, distribution of this important isotope is again increasing and is expected to become heavier than ever as the availability of the new high specific activity material becomes known. The Mg^{28} shipments included one each to Norway and Germany, two to Switzerland, and five each to England and Canada. The increased specific activity will make worldwide shipments even more feasible.

P. RICHARDS, M. GREENE,
J. BARANOSKY, G. WALKER

SPECIAL FABRICATION

A new lead focusing collimator has been designed for collimating low-energy photons into a 5-in. scintillation crystal with maximum sensitivity (at the expense of resolution). The 379 holes are much larger than those in previous collimators and are separated by very thin sections of lead. Two such collimators were fabricated and are being used for radioisotope scanning in the Medical Research Center.

C. KIESLING, P. RICHARDS

RADIOGRAPHY

A total of 2009 radiographs were produced during the year compared with 1631 produced during the same period last year. Radiographic examination included inspecting welds in copper-clad pressure vessel steel, in a new heat transfer loop, and in a large platinum crucible; locating existing conduits and metal objects in concrete floors in the Computer Building and at the HFBR prior to drilling for new conduits; detection of flaws in heavy castings; and quality control on the fabrication of 32 drift-tube stems for the AGS. J. AUSTIN, H. RUGE

NEUTRON GENERATOR

The 14-MeV neutron generator was used for a large number of service irradiations. It was found that the stability of the vacuum, deuterium gas flow, and high voltage can be improved by leaving an expended target in place so that it can be warmed up frequently when it is not otherwise in use; extended idle periods adversely affect the operation. Modifications were made in the shielding room to permit whole-body irradiations of patients for calcium determination by activation analysis. J. AUSTIN

Table 3

Summary of Liquid Waste Operations

	"F" Waste Released to Sewer		
	Gal	Average activity level, Ci/ml	Total activity, mCi
Dec. 26, 1967 to Dec. 25, 1968	971,030	2.46×10^{-12}	9.05
Dec. 26, 1966 to Dec. 25, 1967	1,673,820	4.0×10^{-12}	25.1

Waste Concentrator Operations

	Waste to evaporator ^a	Concentrate ^a	Volume reduction	Activity in mCi	
				Feed	Distillate
1968 ^b	181,690	1,959	93:1	4,494	2.97
1967 ^b	204,675	1,926	104:1	7,361	3.81

"D" Waste Inventory

	Gal start	Gal received	Gal to evaporator	Gal end
Dec. 26, 1967 to Dec. 25, 1968	65,015	167,470	181,690	50,795
Dec. 26, 1966 to Dec. 25, 1967	86,195	183,495	204,675	65,015

^aGallons.

^bNominal years (all other periods are exact years as shown).

LIQUID WASTE OPERATIONS

The inventory of radioactive liquid waste was 50,795 gal at the end of the year compared with 65,015 gal at the beginning. A total of 1959 gal were processed by the waste concentrator during the year. Table 3 summarizes the liquid waste operations.

J. BARANOSKY, A. MACAULAY,
W. AUSTIN, W. GRAY, G. WALKER

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Metallurgy and Materials Science Division

D.H. GURINSKY

This report describes all work sponsored by the Sodium Technology and the Fuels and Materials Branches of the Division of Reactor Development of the US AEC and performed in the Metallurgy and Materials Science Division and the Hot Laboratory Division of the Nuclear Engineering Department of Brookhaven National Laboratory during calendar year 1968.

The work falls into two general areas: corrosion of fast reactor materials by liquid Na and irradiation effects on reactor materials.

Liquid Metal Center

During the year, results were obtained in all areas of the sodium corrosion program for fast reactors: materials testing, sodium physical chemistry and corrosion mechanisms, and analytical chemistry. 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

The current status of the program is given in Table 1. Results of completed 5000-hr tests on four loops (one Zr hot-trapped and three 100°C diffusion cold-trapped) are given in Table 2. Figures 1 and 2 show typical data from two of the four loops; they also show the weight loss as a function of time and temperature, respectively. In general, alloys containing about 40 to 50% total Ni and Cr show the maximum corrosion. Alloys of this class in the program are 47% Fe, 21% Cr, 32% Ni (IN-800) and 31% Fe, 21% Cr, 20% Ni, 2% Co, 3% Mo, 2.5% W (Multimet). Corrosion of 316 SS in these tests was about half that of the preceding alloys, while corrosion of Co-base alloys was 1/2 to 2/3 that of type 316 SS. In general, all the alloys tested showed corrosion rates that decreased with time; the 4000 to 5000-hr rates are shown in Table 2.

Tests in progress on two V-base alloys (V, 21% Ti and V, 15% Ti, 7.5% Cr) and Mo-base alloy (Mo, 0.5% Ti, 0.3% Zr) and pure Mo show that both V-base alloys gain weight in 100°C cold-trapped sodium while the Mo alloy and pure Mo show little or no weight change. The V-base alloys in loop 12-159 (316 SS) gained about 2.5 times the weight the same alloy specimens gained in loop 13-160 (321 SS). The larger weight gains may be due to increased nitrogen and carbon pickup from the 316 SS loop material, since the 321 SS is stabilized by 0.5% Ti. Both alloys show hardened surface layers. The data on V-base alloys are summarized in Table 3.

A comparison of weight gains for the same V-base alloys in thermal convection loops as in a BNL pumped loop (FCL-2, Run 1) circulating at ≈ 22 ft/sec indicates that weight gains in the latter are 3 to 10 times greater than those of the former. This suggests that corrosion of the two V-base alloys tested may be velocity-dependent.

Table 1

Thermal Convection Loop Program Status as of Dec. 1, 1968

Loop No.	Operating time, hr	Loop material	Na condition	Test specimens
1-148 ^a	950	321 SS	165°C cold trap	316 SS; S-1; IN-800
2-149 ^a	24	"	250°C cold trap	UMCO-51; HA-25; Multimet
3-150 ^a	5552	"	Zr hot trap	316 SS; S-1; IN-800
4-151	3879	"	"	HA-25; UMCO-51; HA-25; Multimet
5-152 ^b	2958	321 SS	140°C cold trap 510°C hot leg	Cu-plated 304 SS capsules
6-153	2518	HA-25	100°C cold trap	HA-25; UMCO-51; HA-188 ^c ; S-1
7-154 ^a	24	316 SS	250°C cold trap	321 SS; S-1; IN-800; 304 (Ti)SS
8-155	2273	"	Zr hot trap	321 SS; S-1; IN-800; 304 (Ti)SS
9-156	Pretreat	"	100°C cold trap	HA-25; UMCO-51; HA-188; Multimet
10-157	2347	"	Zr hot trap	HA-25; UMCO-51; HA-188; Multimet
11-158	2251	"	100°C cold trap	321 SS; 304 SS; 304 (Ti)SS; Fe, 15% Cr, 4% Al, 1% Y
12-159	1029	"	"	V, 20% Ti; V, 15% Ti, 7.5% Cr; Mo; Mo, 0.55% Ti, 0.08% Zr
13-160	1412	321 SS	"	"
14-161	1317	"	50 ppm Mg	HA-188; 316 SS; V, 15% Ti, 7.5% Cr; V, 20% Ti
15-162	263	316 SS	100°C cold trap	Fe, Cr, Ni, and Co
16-163	Pretreat	321 SS	175 ppm Li	HA-188; 316 SS; V, 15% Ti, 7.5% Cr; V, 20% Ti

^aCompleted 5000 to 6000-hr run with 100°C cold trap.^bCompleted run.^cOld HA-188 composition, Co, 18% Cr, 18% Ni, 12% W, 1% Fe, 0.1% C.

Table 2

Sodium Corrosion at 760°C in 321 SS Thermal Convection Loops Flowing at ≈ 0.3 ft/sec

Loop No.	Alloy	Weight loss, mg/cm ² , in 5000 hr	Final corrosion rate ^c	
			mg/cm ² hr $\times 10^3$	mils/yr
1-148 ^a	S-1 (Co base), 316 SS, IN-800	0.22	0.04	0.02
		0.94	0.09	0.04
		1.52	0.30	0.12
3-150 ^b	S-1, 316 SS, IN-800	0.40	0.02	0.01
		0.62	0.05	0.02
		1.95	0.23	0.09
2-149 ^a	HA-25, UMCO-51, Multimet	0.87	0.07	0.03
		1.07	0.09	0.04
		1.46	0.13	0.05
7-154 ^d	S-1 (Co base), 316 SS, IN-800	0.60	0.12	0.05
		0.91	0.18	0.07
		1.93	0.38	0.15

^aDiffusion cold trapped at $\approx 100^\circ\text{C}$.^bZirconium hot trapped continuously.^cWeight loss during 4000 to 5000-hr period.^dLoop 7-154 is constructed of 316 SS.

Table 3

Corrosion of Vanadium-Base Alloys in 100°C Diffusion Cold-Trapped Sodium Flowing at ≈ 0.1 ft/sec

Alloy	Loop No.	1000-hr Weight gain, mg/cm ²		Depth of surface layer at 760°C, μ
		730°C	760°C	
V, 20% Ti	12-159 (316 SS)	0.52	0.82	50
V, 20% Ti	13-160 (321 SS)	0.22	-	-
V, 15% Ti, 7.5% Cr	12-159 (316 SS)	0.34	0.55	50
V, 15% Ti, 7.5% Cr	13-160 (321 SS)	0.13	-	-

Figure 1. Corrosion of three alloys in 760°C sodium, hot-trapped with zirconium, and flowing at ≈ 0.1 ft/sec. Thermal convection loop No. 3-150 (321 SS).

The effectiveness of soluble getters in sodium as compared with insoluble Zr in sodium is being evaluated. About 150 to 200 ppm Mg and Li, respectively, have been added to the sodium in loops 14-161 and 16-163. A. FLEITMAN, D. HORNE, B. GALEN

Cobalt Alloy Development Program for Cladding Fuels in 760°C (1400°F) Sodium-Cooled Fast Breeder Reactors

The major objective of this program is to develop a nonembrittling corrosion resistant Co-base tubing alloy, which is to be as strong at 1500°F as 304 SS is at 1200°F and also is to have good resistance to irradiation embrittlement.

Creep Properties. The 1500°F creep-rupture properties of the Co-base alloys in the second phase of the program are given in Table 4; also included are those on HA-188, a new, high-strength commercial tube and sheet alloy that is less susceptible than HA-25 to embrittlement by precipitation of the laves phase, "Co₂W," in the 1200° to 1800°F range.

Figure 2. Effect of temperature on corrosion of three alloys in 100°C diffusion cold-trapped sodium flowing at ≈ 0.1 ft/sec. Thermal convection loop No. 7-154 (316 SS).

The development alloys containing 2 to 3% Ti (Nos. 564 to 568) have 1500°F creep rupture properties that are comparable with the 1200°F rupture properties of 304 SS, thus achieving one of the major objectives of the program. (The 1200°F, 1000-hr rupture stress of 304 SS is around 15,000 psi.) A small increase in the carbon content of these alloys ($\approx 0.10\%$ C) should further improve their 1500°F creep properties.

Tests for Embrittlement and Phase Stability. The effects of long time exposure (1000 hr) at 1400°F upon the room temperature mechanical properties are given in Table 5. The Ti-bearing alloys containing 18% Ni and 0.04% C show extraordinary strength with fair ductility. Alloy No. 567 is particularly outstanding in both strength and ductility. The strengthening effect in the 18% Ni alloys may be due in part to the precipitation of a Ni-Ti compound that is resistant to overaging. The Ti-bearing alloys containing 7 to 10% Ni, 3% Fe, and 0.01% C have both low ductility and low strength, but these alloys have in part undergone transformation to the "low" ductility hexagonal-

Table 4
Co-Base Alloys
(Estimated 1500°F stress for rupture in 1000 hr. Alloys aged at 1500°F for 24 hr.)

Alloy No. ^a	Composition	1000-hr Stress, KSI	Hours of longest test	% Elongation of longest test	Minimum creep rate, %/hr
562	Co, 21% Cr, 7% Ni, 5% Mo, 5% W, 3% Fe, 0.024% C	10	806	11.0	0.010
563	Co, 21% Cr, 10% Ni, 5% Mo, 5% W, 3% Fe, 0.002% C	8	531	11.1	0.010
564	Co, 21% Cr, 7% Ni, 5% Mo, 5% W, 3% Fe, 0.007% C, 2% Ti	12	907	16.1	0.0034
565	Co, 21% Cr, 10% Ni, 5% Mo, 5% W, 3% Fe, 0.007% C, 2% Ti	13	827	7.6	0.004
566	Co, 21% Cr, 10% Ni, 5% Mo, 5% W, 3% Fe, 0.001% C, 3% Ti	14	1026.8	7.2	0.0038
567	Co, 19% Cr, 18% Ni, 12% W, 0.043% C, 2% Ti	16	729.1	2.9	0.0024
568	Co, 19% Cr, 18% Ni, 12% W, 0.044% C, 3% Ti	17	918.6	2.1	0.0012
569 ^b	Co, 19% Cr, 11% Ni, 14% W, 1% Fe, 0.10% C	13	1074.8	14.4	0.0045
HA-188	Co, 22% Cr, 22% Ni, 14% W, 0.1% C	16	886	32.4	—

^aAlloys Nos. 562, 563, 564, 565, and 569 solution treated at 2050°F. Alloy No. 566 solution treated at 2150°F. Alloy Nos. 567 and 568 solution treated at 2250°F.

^bHA-25 alloy. Composition has been adjusted slightly in an attempt to reduce high temperature embrittlement.

close-packed phase of cobalt. Apparently there is an insufficient amount of face-centered-cubic stabilizing alloy elements (Ni-Fe-C) in these alloys. Alloy No. 566 of this group, which has the lowest ductility, has a nearly continuous grain boundary precipitate.

Alloy No. 569, a HA-25 alloy composition modified in an attempt to minimize "Co₂W" embrittlement, has fair ductility, and the new commercial alloy HA-188 has good to excellent ductility.* Alloy No. 563, which contained no Ti or C and only 7% Ni, showed good ductility but has the lowest 1000-hr stress for rupture at 1500°F.

Microstructure. Efforts to identify the precipitates and phases present in the alloys are in progress. Optical metallography, electron microscopy, and microprobe analysis of the specimens have been performed. X-ray diffraction studies and chemical analysis on residues extracted electrolytically from the bulk specimens are also being utilized. At least two phases are present — one is rich in Ti and low in cobalt, and the second is rich in W and Co.

The matrices of alloys Nos. 562 to 566 in the aged condition have been found to contain some HCP cobalt phase. This phase is less ductile than FCC cobalt, and indicates that these alloys require more cubic stabilizers.

*Numerous tests at Union Carbide Corp. indicate that some heats of HA-188 become embrittled by "Co₂W" precipitation after long exposure to 1400° to 1800°F.

New Alloys. A third group of eight alloys, containing 0.1 to 0.6% Ti have been prepared in an effort to produce an alloy that is more resistant to radiation embrittlement. Nominal base compositions are (1) Co, 21% Cr, 10% Ni, 8% Fe, 5% W, 5% Mo, 0.03% C*, and (2) Co, 22% Cr, 22% Ni, 14% W, 0.03% C. Each alloy base is prepared with titanium at nominal levels of 0.1, 0.2, 0.4, and 0.6% Ti.

Slow strain room temperature tensile tests of irradiated material from alloys based on the first composition showed excellent ductility. These tests are discussed in detail in the section on irradiation effects.

A. FLEITMAN, D. HORNE

Forced Circulation Loops

High velocity corrosion studies are being carried out in two forced circulation loops (FCL-1 and FCL-2), fabricated entirely of stabilized stainless steels, in which specimens are exposed to Na in a 24-in.-long, rising temperature region. The specimens are periodically removed from each loop through an inert atmosphere glove box, cleaned by vacuum-distilling the residual Na, rinsed in alcohol, and measuring their weight changes by metallographic examination and by x-ray fluoroscopy. The loops are of the "figure-of-eight" type, with a double-pipe heat economizer that ex-

*The iron has been increased from 3 to 8% in order to prevent any transformation of cobalt to HCP.

Table 5

Room Temperature Tensile Properties^a of Co-Base Alloys Aged at 1400°F for 1000 hr After Solution Anneal and Water Quench

Alloy No.	Solution anneal temperature	Ultimate tensile strength, KSI	Yield strength, 0.2% KSI	% Elongation
562	2250°F for 15 min	93	57.5	13
563		103.8	56.6	26
564		94	64.2	4
565		108.3	67.8	7
566		104.5	80.8	3
567		157.2	115.0	13
568		160	131.3	6
569		121.2	75	15
HA-188		152.3	70.3	41
562	2050°F for 15 min	96	70	6
563		112.2	63.3	24
564		103.8	80.3	3
565		101	71.6	4
566		98.3	94.1	1
567		177	125.8	17
568		190.6	152.5	8
569		123.3	81.6	8
HA-188		148.8	74.2	24

^aStrain rate of 0.001 in./in./min.

changes a major portion of the heat. The bulk of the heat is generated in the preheater and test section regions by low voltage, high current resistance heating of pipe, sodium, and specimens. Heat is removed by finned air blast coolers. Two electromagnetic pumps and a flowmeter are included in the cold leg. Side circuits include a cold trap and a hot trap for oxygen control, a plugging meter to estimate oxygen concentration, electrochemical oxygen meters to determine the oxygen activity in the sodium, and sodium sampling devices.

A schematic drawing of the test section is shown in Figure 3; high sodium velocity is achieved in the flow annulus created by the test section and the outer containment. This 0.049-in. annulus is maintained by 0.045-in.-high centering guides located every 3½ in. along the test section on the uncoupling joints (shaded sections). There are 60 tubular specimens of which about 50 are in the rising temperature region and about 10 are in the (isothermal) downstream region. Each specimen is 0.486 in. in diam × ½ in. long × 0.030 in. thick.

Figure 3. Forced circulation loop test section.

Table 6

Nominal Compositions of Test Materials for FCL-1, Run 2

Alloy	Composition, wt %
HA-25	Co, 20% Cr, 10% Ni, 15% W, 3% Fe
UMCO-51	Co, 28% Cr, 19% Fe, 2% Nb, 0.3% C
HA-8188	Co, 19% Cr, 18% Ni, 12% W, 2% Fe
321 SS	Fe, 17% Cr, 10% Ni, 0.3% Ti
304 SS	Fe, 19% Cr, 19% Ni, 0.08% C
304L (Ti) SS	Fe, 10% Cr, 11% Ni, 0.2% Ti, 0.01% C
TV-20	V, 20% Ti
D-11	Nb, 1% Zr
TZM	Mo, 0.5% Ti, 0.06% Zr
VTiCr	V, 15% Ti, 7.5% Cr
VCrTi	V, 15% Cr, 5% Ti

The test section is ≈36 in. long. The nominal compositions of the alloys tested in this program are given in Table 6.

FCL-1. A 1655-hr test run with ≈4 ppm oxygen in the Na was concluded and a 647-hr portion of a second test run at ≈12 ppm oxygen* in Na has also been completed. The materials evaluated and the test conditions of these runs are given in Table 7. At the conclusion of the run with 4 ppm O, eight of the HA-25 and four of the Mo specimens were removed from the test section and replaced by six specimens each of HA-8188 and type 304L(Ti) stainless steel. The other specimens were not replaced by new specimens at the end of the run.

The weight change measurements are plotted vs time at 760° and 710°C for the HA-25 alloy and the 304 SS specimens in Figure 4 and for the UMCO-51 alloy and 321 SS specimens in Figure

*During the 647-hr incremental run, continuous additions of oxygen had to be made to the loop by flowing Na in a branch circuit through an additive vessel containing Na₂O in order to maintain this concentration level.

Table 7
FCL-1 Operating Conditions (12/1/68)^a

Loop No.	Test time, hr	Type of run	Test section materials	Range of oxygen, ppm
FCL-1, Run 1	1A = 168	Cold trap	HA-25	2 to 6
			UMCO-51	
	1B = 336		321 SS	
			304 SS	
	1C = 600		Molybdenum	
	1D = 551			
Total = 1655				
FCL-1, Run 2	2A = 192	Cold trap	HA-25 ^b	8 to 18
			UMCO-51 ^b	
			321 SS ^b	
			304 SS ^b	
	2B = 455		Molybdenum ^b	
			HA-8188	
			304L(Ti)	

^aLoop material, 321 SS; max temperature = 760°C, test section velocity = 22 ft/sec, loop ΔT = 200°C.

^bThese specimens aged in Run 1 and were not exchanged for new specimens in Run 2.

5. The calculated corrosion rates (mils/yr) for the last incremental run at the two oxygen levels are also shown. The corrosion rates of 304 and 321 SS show a near-linear dependence on the oxygen concentration in sodium. HA-25 and UMCO-51 do not show this dependence, and the corrosion rate of HA-25 actually decreased with increased oxygen. The unalloyed molybdenum specimens exhibited very little weight change. The two new sets of specimens also tested at this time, 304L(Ti) and HA-8188 (Co-base), underwent the normally high weight loss usually observed during the initial phase of the corrosion process. These results are preliminary at this time and are therefore not included in the report.

The corrosion results for each material show a linear relationship when plotted as log corrosion rate vs reciprocal temperature. For the results of 4 ppm O in Na, the slope for HA-25 was greatest, equivalent to an over-all activation energy of ≈ 44 kcal, and that for type 304 SS smallest, ≈ 27 kcal. The results of 12 ppm O in Na may not have reached steady state yet. The corrosion rates for

the 304 and 321 SS are plotted vs reciprocal temperature ($1/T$, °K) in Figure 6, and are compared with the United Kingdom data and the General Electric corrosion equation. At a given oxygen level, all the data seem to be in reasonable agreement.

In every case, downstream specimens showed slightly lower corrosion rates than those of the specimens at the same temperature in the rising temperature region.

Throughout the test, specimens of the alloys were analyzed by x-ray fluorescence. The results of the analysis of the 750°C specimens of HA-25 and 304 SS are shown in Figure 7. During the 1655-hr low oxygen run, the stainless steels showed Fe enrichment and Ni, Cr, and Mn depletion. The change in composition increased with temperature and exposure time. Similarly, the Co-base alloys showed depletion of Cr, Ni, and Mn, and enrichment of Co, Fe, and W. The data are plotted as ratio of counts of an element at the specimen surface to that of an unexposed specimen. Hence, values of >1 indicate enrichment and values of <1 indicate depletion.

When the oxygen content of the Na was increased, the degree of enrichment and depletion of the constituents of 304 SS decreased. Similar results were observed with respect to W, Co, and Cr in the HA-25. However, the most striking change was the degree of enrichment of Fe on the surface of HA-25; the ratio of counts increased from 1.5 at the conclusion of the low oxygen run to 6.8 after 647 hr at the high oxygen level.

Preliminary metallographic examination of HA-25 after the 12 ppm oxygen run showed that the surface of the specimen is porous to a depth of ≈ 6 to 8 μ . There appears to be nonadherent particulate material on the surface which may be due to deposition. Further identification of this material is in progress. The 10 to 15 ppm oxygen in Na corrosion run will be resumed.

FCL-2. A 2004-hr test run has been concluded with this loop under Zr-hot-trapped conditions, and a 261-hr portion of a second test run with ≈ 4 ppm oxygen in Na has also been completed.

The operating conditions and materials tested are given in Table 8. During the hot-trapped run two electrochemical oxygen meters and amalgamation analyses confirmed the low oxygen level (<1 ppm).

The weight change measurements of the materials tested in the Zr-hot-trapped run can be summarized as follows.

Figure 4. Effect of oxygen on corrosion rate of HA-25 and 304 SS (velocity = 22 ft/sec).

Figure 5. Effect of oxygen on corrosion rate of UMC0-51 and 321 SS (velocity = 22 ft/sec).

Figure 6. Comparison of corrosion rates of stainless steels vs reciprocal temperature.

Figure 7. X-ray fluorescence results (FCL-1).

Table 8				
FCL-2 Operating Conditions (12/1/68) ^a				
Loop No.	Test time, hr	Type of run	Test section materials	Range of oxygen, ppm
FCL-2, Run 1	1A = 335	Hot trap	V-20 Ti	<1
			V-15 Ti-7.5 Cr	
	1B = 675		V-15 Cr-5 Ti	
			Nb-1 Zr	
	1C = 322		Mo-TZM	
			321 SS	
	1D = 672			
	Total = 2004			
FCL-2, Run 2	2A = 261	Cold trap	^b	≈5
	2B = 120 ^c			

^aLoop material, 321 SS; max temperature = 760°C, test section velocity = 22 ft/sec, loop $\Delta T = 200^\circ\text{C}$.

^bThese specimens aged in Run 1 and were not exchanged for new specimens in Run 2.

^cIn progress.

Table 9			
Weight Loss Measurements of Materials Tested in FCL-2, Run 2A			
Oxygen (amalgamation), ≈5 ppm			
Oxygen (UNC meters), ≈3 ppm			
Velocity, 22 ft/sec			
Temperature range, 710° to 760°C			
Exposure time, 261 hr			
Material	Condition	No. of specimens	Weight loss, mg/cm ²
Nb, 1% Zr	Aged	6	25
	New	2	37
V, 20% Ti	Aged	6	6.6
	New	2	11
V, 15% Ti, 7½% Cr	Aged	12	7.8
	New	2	6
V, 15% Cr, 5% Ti	Aged	6	6.6
	New	2	6
Mo-TZM	Aged	6	<0.05 (gain)
	New	2	
321 SS	Aged	6	0.14 ^a
	New	2	1.0 ^b

^aEquivalent to ≈0.2 mils/yr.

^bEquivalent to ≈1.5 mils/yr.

Figure 8. Cumulative weight change data of vanadium-base alloys and Nb-1% Zr.

1. The V- and Nb-base alloys all gained weight; the initial weight gain was high but lower steady-state rates were attained as shown in Figure 8. The steady-state rates for all the V-base alloys were essentially the same.

2. Only a slight temperature effect was observed on most of the alloys. The Mo-TZM specimens gained negligible weight as did the Mo specimens in FCL-1.

3. The 321 SS specimens lost weight; their steady-state corrosion rate was slightly higher than those in FCL-1 (4 ppm oxygen run). Post-test metallographic and chemical analyses of the two sets of specimens may explain the apparent weight change discrepancy.

After the oxygen level was raised to ≈4 ppm in this loop, all the V-base alloys and Nb-1% Zr exhibited very high weight losses (see Table 9). Once again, the Mo-TZM alloy was relatively unaffected. The 321 SS specimens showed weight losses comparable with results obtained in FCL-1, Run 1.

In summary, it has been shown that Co-base alloys have corrosion rates roughly equivalent to stainless steel in the 710° to 760°C temperature range in high-velocity, low-oxygen sodium (≈4 ppm). On a strength-to-corrosion rate basis, the Co alloys would be favored. High initial corrosion rates of up to 3.5 mils/yr after 200 hr decrease rapidly and approach steady-state values. These high rates are believed to be due to rapid leaching of Ni, Cr, and Mn from the surface of the specimens as shown by x-ray fluorescence analysis of the corroding surface.

Figure 9. Schematic diagram of Heater Test Loop.

In addition, preliminary results show that the Co-base alloys appear to have better corrosion resistance to Na containing 12 ppm oxygen than the stainless steels do. However, the possibility of Fe deposition on the surface of the Co alloys exists which would certainly complicate corrosion measurements. Prolonged testing under these conditions should reveal whether the corrosion rate or the Fe deposition rate will be predominant under steady-state conditions.

V-base alloys and Nb-1% Zr are very sensitive to oxygen in the Na as evidenced by weight gains observed under hot-trapped (<1 ppm O) conditions and extremely high weight losses found in a well cold-trapped (≈ 4 ppm O) run.

A. ROMANO, S. WACHTEL, W. TREMEL

High Heat Flux Corrosion Loops

Construction of the Heater Test Loop (HTL) was completed. This loop is to be used to test high flux heaters and to develop appropriate test section configurations for use with the heaters.

Medium frequency (10 kHz) induction heating is being tested first. A 50-kW, 10-kHz motor-generator type induction heater was purchased and installed. Because of the potential hazard of using a water-cooled induction coil in close proximity with hot sodium, a NaK coolant system has

Figure 10. Schematic diagram of the induction heated test section in the Heater Test Loop.

been substituted. Construction of the NaK coolant loop was completed and a test section for the HTL was designed, fabricated, and inserted into the loop.

Figure 9 shows a layout of the HTL, and a schematic diagram of the test section is shown in Figure 10. Heat is generated in the $\frac{5}{8}$ -in.-o.d. $\times \frac{1}{2}$ -in.-i.d. HA-25 tube as well as in the specimen holder. Coolant sodium passes at high velocity (≈ 20 ft/sec) through the test section which contains the 0.315-in.-i.d. $\times 0.015$ -in.-thick specimens. In order to minimize the outside wall to Na temperature gradient, the specimen holder in the region of the induction coil is fabricated of a magnetically soft alloy, 2-V Permendur (49% Co, 49%

Figure 11. Typical temperature profile along induction heated test section showing wall, specimen, and sodium temperatures at a 1×10^6 Btu/hr-ft² nominal heat flux.

Fe, 2% V) which has an extremely high saturation value (23,000 G). This material serves to concentrate the lines of force induced by the heater directly behind the specimens, thus increasing the proportion of heat generated in that region. For a constant heat generation, the smaller distance that the heat must be transported (i.e., to the Na), the smaller the ΔT driving force required.

After filling and circulating NaK in the coolant loop, the induction generator was operated at very low power to supply heat in the test section region, and the HTL was then filled. With sodium circulating at 3 to 5 gpm, the induction heater was operated over a wide range of power levels at a number of sodium temperatures. Nominal heat flux levels in the test section of 1.0×10^6 Btu/hr-ft² were reached at $\approx 600^\circ\text{C}$ Na temperature ($\approx 650^\circ\text{C}$ specimen temperature) and 0.6×10^6 at $\approx 700^\circ\text{C}$ Na temperature ($\approx 720^\circ\text{C}$ specimen temperature).

Figure 11 is a typical temperature profile for a high flux run, in which the outside wall, bulk Na inlet and outlet, and Permendur temperatures are all plotted vs location. Local heat fluxes, estimated as proportional to the ΔT (outside wall to Na), are

Figure 12. ΔT , outside wall to flowing sodium vs nominal heat flux for induction heating test runs.

also shown. Over-all nominal heat flux for this run was 1.07×10^6 Btu/hr-ft².

Figure 12 shows maximum outside wall temperature, located 2 in. below the top of the induction coil, vs nominal heat flux (total heat input from Na temperature rise divided by high flux specimen surface area - 10 in. long $\times$ 0.315 in. in diam). An almost linear relation between these two variables is shown. At 1.0×10^6 Btu/hr-ft² heat flux, a maximum temperature gradient of 260°C from the outer wall to the flowing sodium is generated.

High induction coil temperatures, resulting from the use of a swaged copper-over-stainless steel induction coil, were anticipated to be a possible source of operational difficulty. A conventional all copper coil could not be used with NaK coolant. Because of nonmetallurgical bonding between copper and stainless steel, high temperatures could result from poor transfer to the NaK of I²R heat generated within the copper. However, it has been found that, even at 1×10^6 Btu/hr-ft², or ≈ 22 kW generated in the test section, induction coil temperatures have not exceeded 160°C .

The use of the 18-in.-diam $\times$ 19-turn stainless steel choke coil to provide a high electrical impedance path for the recirculating NaK coolant has been extremely effective. Initial results for cir-

Table 10
Heater Test Loop
Operating Conditions, Run 4M

Heat input	22 kW
Nominal heat flux	$1.0 \text{ to } 1.1 \times 10^6$ Btu/hr-ft ²
Time of continuous operation	230 hr
Na velocity in test section	20 ft/sec
Estimated max specimen temperature	660°C
Na inlet temperature	535°C
Na outlet temperature	605°C
Max wall temperature	860°C

culating water have been verified with the NaK system.

An extended period of operation at high heat flux (1.0×10^6 Btu/hr-ft² or higher) has been started using a maximum specimen temperature of $\approx 650^\circ\text{C}$ ($\approx 1200^\circ\text{F}$). Operating conditions are given in Table 10. S. WACHTEL, A. ROMANO, J. BRANDON

SODIUM SOLUTION CHEMISTRY AND CORROSION MECHANISMS

J. WEEKS, L. NEWMAN

The objective of this program is to develop an understanding of the physical chemistry of sodium coolants and its relation to the chemical and kinetic aspects of corrosion processes in sodium.

Solubility Studies

The solubilities of nickel and iron in sodium are being measured as part of a continuing program on obtaining the solubilities of LMFBR materials.

The basic apparatus designed to determine the solubilities of various metals in sodium was described in the 1967 Annual Report [BNL 50082 (S-70)].

The experimental equipment was modified during 1968 to include an "air-lock" sampling port (Figure 13) that fits the top of the experimental vessel. The sampling cups are introduced through a ball valve into a chamber capable of being evacuated and pressurized with purified helium prior to immersion of the cups into the Na melt through a lower ball valve. The sampling port permits greater flexibility than heretofore possible. The Na may be further oxygen-gettered with U or doped with a desired constituent at any point dur-

Figure 13. Sodium solubility apparatus (modified).

ing an experiment. In addition, molybdenum sampling cups have now been prepared by boring out 1/2-in.-diam Mo rod. The cups are suspended via thin Mo wires into the Na melt. The many difficult welding operations required in the past to prepare cups from sheet stock have thus been eliminated. The surfaces of the new cups are smooth and no longer interfere with the proper transfer of cup contents. These cups are cleaned with aqua regia and then rinsed in 6 N HCl until Fe leaching results are below the analysts' detection limits.

Nickel. Preliminary nickel solubility experiments at temperatures between 340° and 420°C produced widely scattered results. This scatter presumably resulted from two causes: the melt was alternately heated or cooled to the equilibration temperatures, possibly causing particulates to form; and the analytical blank was of comparable magnitude to the Ni solubility. The Ni solubility in this region as extrapolated from our higher temperature runs must be < 0.5 ppm.

Nickel solubility measurements at temperatures from 446° to 600°C are shown in Figure 14. In this series of runs, each equilibration temperature was higher than the previous temperature and many replicate samples were submitted for analy-

sis at each temperature. The 600°C Ni run was repeated because the first run was actually equilibrated at 500°C for 24 hr and sampled immediately after raising the temperature to 600°C instead of the usual equilibration period at this temperature. The value for nickel for this run fits well with results at 500°C. The solubility may be calculated using the following equation:

$$\text{Ni}(\text{ppm}) = 0.0046T(^{\circ}\text{C}) - 1.40$$

Iron. The results of the first reproducible iron runs that are above the analytical detection limits are given sequentially in Table 11. Sample weights for all runs were 1.5 to 2 g. The first runs, in which the oxygen levels were kept relatively low, basically duplicate the low solubility results obtained previously at slightly lower temperatures. The Fe solubility measured in these runs is in excellent agreement, and averages 0.3 ppm.

The same sodium melt was then doped with Na_2O_2 to raise the oxygen level to 460 ppm. Two series of samples were then taken. Iron solubilities increased by a factor of ≈ 6 to 1.9 ppm, and were in excellent agreement, even though the melt was kept at room temperature for several days between the two runs.

The same sodium melt was then gettered with uranium foil to reduce the oxygen to 220 ppm; the Fe was at the same time reduced to a maximum of 0.4 ppm. The surface of the uranium foil was found essentially free of Fe^{59} ; the iron solubility must therefore be a function of the oxygen content.

The wet chemical iron content throughout the series of experiments remained unaltered at ≈ 3

ppm. This value is essentially the same as that found on analysis of sodium freshly distilled into quartz and molybdenum containers, and corresponds to ≈ 50 to 100% of the analytical blank.

The sodium was then increased in oxygen content from 220 ppm to saturation by the addition of 1% oxygen as Na_2O_2 . The Fe^{59} concentration again increased to 10.5 ppm, thus reaffirming an oxygen dependence. At this point the temperature was elevated to 525° and 575°C with samples taken at each temperature. Fe^{59} values increased to 50 ppm at 575°C. Additional samples were taken at 575°C over a period of one week. These runs showed continued large increases in iron concentration. Finally, the experiment was dismantled and the residue at the bottom of the iron crucible was found to contain large quantities of Fe^{59} . However, the wet chemical analyses of the high-oxygen samples were lower than the radiochemical results in all cases. These results obviously do not represent true liquidus values. The iron solubility results for run II (550°C) are also shown in Table 11. In all cases the changes in the amalgamation results for oxygen agreed reasonably well with the added or gettered quantities of Na_2O . After an oxygen activity of 0.2 was reached, the Fe^{59} values increased to ≈ 4 ppm at the saturation value, as seen in Figure 15. The wet chemical iron results were occasionally up to an order of magnitude greater than the radiochemical results. However, their relative constancy as the radiochemical Fe changes (by oxygen additions and removals) implies that a major part of this iron may be due to contamination during subsequent handling.

Extrapolation of iron solubility results to essentially zero oxygen yields solubility values of 0.3 and 0.85 at 486° and 550°C, respectively. Figure 16 shows this information plotted vs reciprocal temperature. Recent results from Thorley and Tyzack (*Alkali Metal Coolants*, p. 97, IAEA, 1967) and Eichelberger and McKisson (AI) are also included. The low oxygen iron solubility results yield a straight line where the solubility may be calculated from the expression $\log_{10}(\text{ppm Fe}) = 7.05 - 5730/T(^{\circ}\text{K})$. J. WEEKS, R. SINGER, W. BECKER, J. SAULS

Figure 14. Solubility of nickel in sodium as a function of temperature.

Chemical Nature of Impurities in Sodium

These studies are directed at obtaining thermodynamic and kinetic information on sodium-impurity metal reactions, including equilibrium con-

Table 11

Solubility of Iron in Sodium

Run No.	Temp., °C	No. Fe ⁵⁹ samples	Fe ⁵⁹ avg., ppm	Fe ⁵⁹ range, ppm	Oxygen, ppm	Wet chemical ppm
I	482	5	0.33	0.13–0.62	~50 ^a	3–7
	482	5	0.27	0.10–0.56	~50 ^a	3–4.5
	486	8	1.8	1.3–2.9	460 ^a	2.6–4.2
	486	6	2.0	1.1–4.0	460 ^a	1.2–7.6
	486	6	≤0.4	0–0.4	220 ^b	3.1
	486	2	10.5	9.1–11.9	1035 ^c	–
	525	3	29.0	28.5–29.4	1490 ^c	–
	575	2	52.1	50.3–53.8	2250 ^c	34–35
	575	1	80	80	2250 ^c	62
	575	2	162	158–166	2250 ^c	73
	575	2	146	137–155	2250 ^c	–
	575	2	685	320–1050	2250 ^c	–
	550	1	0.09	–	<1 ^d	7.3
	550	2	0.66	0.57–0.75	85 ^e	–
	550	2	0.73	0.31–1.1	340 ^e	–
II	550	2	1.54	1.44–1.64	570 ^e	2.1
	550	2	1.51	1.40–1.62	1000 ^e	4.1
	550	2	2.8	2.5–3.1	1600 ^e	13
	550	2	3.6	3.5–3.7	1800 ^f	4.2
	550	1	4.2	–	2040 ^e	–
	550	2	1.1	0.43–1.8	131 ^b	–
	550	2	0.87	0.80–0.93	72 ^b	–
	550	2	0.61	0.44–0.78	50 ^d	–
	550	2	1.07	0.83–1.3	25 ^d	–

^aAmalgamation result, oxygen added as Na₂O₂.^bAmalgamation result, oxygen removed by gettering with uranium.^cSaturated values interpolated from Eichelberger's estimate. 1% oxygen was added as Na₂O₂.^dEstimated by uranium gettering technique.^eAmalgamation result, oxygen added as Na₂O.^fEstimated from weighed addition of Na₂O. Amalgamation sample lost.

Figure 15. A logarithmic plot of the solubility of iron in sodium as a function of oxygen activity. The extrapolations to zero oxygen are 0.3 ppm Fe at 486°C and 0.58 ppm Fe at 550°C.

Figure 16. Recent data on the solubility of iron in low-oxygen sodium.

stants, 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 sodium or on surfaces in contact with it will also be studied to provide insight into reaction mechanisms, and to aid in interpretation and/or development of chemical analysis methods.

Studies on Sodium-Oxygen Chemistry. The corrosion rates of many metals in sodium are dependent on the concentration of oxygen. To obtain a more detailed knowledge of these corrosion mechanisms, studies are being made of the thermodynamics and solubility of the sodium-oxygen system and reactions between oxygen and impurities, metallic and nonmetallic, in sodium. The emf developed by a solid electrolyte galvanic cell is used to measure free energy and to monitor the changes in oxygen activity resulting from these reactions.

Initial tests were conducted in stainless steel systems at temperatures between 300° and 400°C with the use of a commercial oxygen meter electrode with a Cu,Cu₂O reference electrode. Sodium oxide pellets were usually used to increase oxygen concentration or activity. Uranium foils were used to getter oxygen; the rate of this reaction was used to determine the oxygen concentration in sodium and to calibrate the oxygen meters. The results showed that one or more substances present in the stainless steel system react with oxygen to buffer the oxygen activity in the sodium. Thus, the stainless steel appears capable of acting as a source or sink for oxygen depending on the oxygen activity in the sodium. A more detailed investigation of these

reactions was undertaken to determine the particular substances involved and the conditions under which reactions occur.

In these tests the Cu,Cu₂O electrode in the commercial oxygen meter was replaced with a Na,Na₂O reference electrode, which was developed to overcome the limitations on operating temperature of the commercial meter. The Na,Na₂O electrode can be used at temperatures to 550°C. Furthermore it appears to be more reversible and less subject to contamination than the Cu,Cu₂O reference electrode, and is not affected by normal variations at ambient temperature. However, the ceramic electrolyte tubes cracked after a few weeks of operation at 500° or 550°C.

Free energy data for chromium oxides, sodium oxide, and sodium chromite suggest that chromium should react with oxygen in sodium in the temperature and concentration ranges of interest in this study. Accordingly a series of tests were conducted in which two grams of a mixture of chromium and chromium oxide (Cr₂O₃) were added to ≈300 g of sodium contained in a heavily oxidized zirconium beaker.

When the system was heated to 500°C and allowed to stabilize, a cell potential of ≈154 mV was observed in one case and 161 mV in a duplicate setup. This potential was characteristic of the system, i.e., the cell potential tended to return to this value (see Figure 17). If the oxygen activity of the system was displaced by immersing uranium foil in the sodium (curve B), the potential increased; when the uranium foil was removed, the cell potential returned to the original value of 154 or 161 mV. Similarly, when a small quantity of oxygen was added as Na₂O (curve C), the cell potential decreased, but then returned to the original potential. After large quantities of oxygen were added (curve D) or removed (curves A and B), the potential changed to a much smaller extent but towards 154 mV. Curve A also indicated that at 230 mV a steady state was reached when the oxygen concentration did not change and the rate of removal of the oxygen by uranium was equal to the rate of decomposition of source of oxygen.

This behavior suggests that a material, probably Cr, exists in the system that can act as either a source or sink for oxygen, and it tends to maintain the system at a constant oxygen activity (buffered system) equivalent to 154 to 161 mV. Threshold oxygen concentration for this reaction at 500°C,

Figure 17. The behavior of the potential of the cell Na,Na₂O | ThO₂-15 wt % Y₂O₃ | Na(Cr + Cr₂O₃) on addition and removal of oxygen.

based on uranium foil calibration of the oxide meters, is ≈ 17 ppm.

Measurements of the solubility of oxygen in sodium have been obtained by a new method that is independent of conventional sampling and analytical techniques. The oxygen solubility vs temperature relationship can be derived from emf measurements on the cell

with the use of the uranium gettering technique to determine oxygen concentration ($\text{Na}_2\text{O}_{\text{dis}}$) at the unsaturated electrode. The emf of this cell, assuming a transference number of one (see section C-1-a) and Henry's law is:

$$E = \frac{2.3RT}{2f} \log C_0 - \frac{2.3RT}{2f} \log C, \quad (1)$$

where R = gas constant; T = cell temperature, $^{\circ}\text{K}$; f = Faraday constant; C = concentration of oxygen in sodium; and C_0 = solubility of oxygen in sodium at T . Equation (1) can be rearranged to give

$$\log C = \log C_0 - \frac{2f}{2.3RT} E. \quad (2)$$

The reference electrode was calibrated at several temperatures using the uranium gettering technique. The intercept of a plot of $\log C$ vs E at zero potential gives the solubility of oxygen at the cell temperature.

The solubility relationship was also derived from independent measurements of cell emf vs temperature at constant concentration. Substituting the solubility relationship

$$\log C_0 = A + (B/T) \quad (3)$$

and

$$\alpha = 2.3R/2f = \text{constant}$$

into Eq. (1) and differentiating with respect to T at constant oxygen concentration yields

$$(\partial E / \partial T)_C = \alpha A - \alpha \log C \quad (4)$$

and

$$E = (\partial E / \partial T)_C T + \alpha B. \quad (5)$$

A plot of E vs T gives a straight line with slope equal to $(\partial E / \partial T)_C$. The slope of the solubility equation (B) can therefore be calculated from measured E vs T data using Eq. (5). The oxygen concentration, determined by the uranium getter-

ing technique, is then used in Eq. (4) to calculate the value of A . The procedure can be repeated at several oxygen concentrations to yield replicate determinations of the solubility constants A and B .

These two methods [i.e., zero intercept and $(\partial E / \partial T)_C$] give a preliminary solubility relationship of

$$\log C_0(\text{ppm}) = 6.55 - (2600/T) \quad (6)$$

for temperatures above 350°C . This equation gives values of oxygen solubility slightly greater than those given by Eichelberger's correlation (AI-AEC-12685). They are in agreement with experimental data obtained at temperatures above 350°C .

The variation of the emf with temperature shows marked inflections below about 370° which could result from a phase transformation of the Na_2O . A low energy phase transformation has been reported by R.T. Grimley and J.L. Margrave [*J. Phys. Chem.* **64**, 1763 (1963)] in the temperature range 230° to 530°C . A phase transformation in sodium would indicate a higher oxygen solubility at low temperatures than those obtained from extrapolation of the high temperature data. This may be an explanation of the observed break in the solubility curves at about 300°C observed by a number of investigators [K.T. CLAXTON, *J. Nucl. Energy* **21**, 351 (1967)]. H. ISAACS, B. MINUSHKIN, W. BECKER, V. WILLIAMS

Sodium-Gas Reactions - Hydrogen-Bearing Gases. Studies on the reaction of liquid sodium with both hydrogen- and carbon-bearing gases are in progress, with a view to obtaining basic information on sodium-nonmetal systems. The method consists of following pressure changes as small quantities of the gas are absorbed by a large excess of liquid sodium.

The reaction of hydrogen chloride (*ca.* 10 cm Hg) with excess liquid sodium was shown to proceed in the following two distinct steps in the 100° to 250°C range:

Hydrogen is produced quantitatively in the gas phase, according to (1), prior to its reaction to produce NaH; no hydrogen, atomic or molecular, is held by the sodium until all the hydrogen chloride has reacted. Addition of 5 at. % barium to the sodium was found to alter the rate of both steps.

Step (2), found to be first order with respect to hydrogen, was greatly accelerated in the presence of barium; on the other hand, removal of hydrogen chloride from the gas phase (step 1) was slowed down drastically. Similar observations were made in the presence of calcium.

In the reaction of hydrogen chloride with sodium containing barium, barium chloride was the predominant product. The slower hydrogen chloride uptake, in the temperature range 160° to 240°C, was shown to obey a relationship consistent with the assumption that (1) barium chloride forms highly protective surface films on the liquid Na, and (2) the reaction proceeds only via HCl diffusion down "leakage paths" (cracks and pores) in the product layer.

The reaction of HCl (step 1) is therefore considered to be controlled by processes of a physical nature with both pure sodium and sodium-barium alloy. On the other hand, in the reaction of hydrogen (step 2) the controlling step is considered to involve "chemical" interaction of hydrogen molecules with the liquid metal, explaining the contrasting effect of barium on the two stages of the over-all reaction.

The reaction of hydrogen with sodium containing 18 ppm oxygen at 400°C was studied by measuring the decrease in hydrogen pressure as a function of time. The oxygen activity in the sodium was measured continuously with the electrochemical oxygen meter.

The hydrogen pressure was found to fall exponentially with time, indicating a first-order reaction with respect to molecular hydrogen. Accompanying this uptake of hydrogen was a simultaneous decrease in oxygen activity in the sodium.

These preliminary results suggest that, when hydrogen reacts at 400°C, neither hydrogen dissolution or diffusion in the liquid sodium are rate-controlling; rather, the rate-determining step involves dissociation of the H₂ molecules at the sodium surface. They also suggest that hydrogen and oxygen interact in solution to reduce the oxygen activity at constant oxygen concentration, and that this interaction is rapid compared with the initial H₂ reaction.

Sodium-Gas Reactions – Carbon-Bearing Gases.

The reaction of cyanogen with excess liquid sodium,

was studied to gain an idea of the solubility of sodium cyanide in liquid sodium. By visual obser-

vation of the gradual disappearance of a thin film as the temperature was raised stepwise from 120° to 250°C, it was concluded that the solubility of sodium cyanide in liquid sodium is <5 ppm at 250°C.

Studies on the interaction of carbon monoxide with excess liquid sodium have been initiated, primarily to ascertain whether carbon monoxide or sodium-carbon monoxide reaction products have finite solubilities in the liquid metal. In preliminary experiments carbon monoxide has been reacted with a large excess of vigorously stirred sodium, particular attention being directed to the nature of the initial reaction and to the formation and disappearance of product films on the liquid metal surface. In a typical experiment, at 200°C, the initial absorption took place in three steps: (i) an initial induction period of about 1 hr, (ii) a rapid absorption stage, and (iii) a slow stage where the reaction rate again becomes negligible. On contact with CO (at 60 cm Hg), a purple film was formed on the initially bright metal surface [step (i)]. This film disappeared during the rapid absorption stage [step (ii)], and the metal surface again appeared bright and clean. The pressure drop during step (ii) was <20%; no change in the nature of the metal surface or CO pressure was detected after leaving the system for several hours. However, when the residual CO was pumped off (at 200°C) a grey-purple precipitate appeared instantaneously on the metal surface. M. HOBDELL,

H. ISAACS

Sodium Chemistry Loop

The sodium chemistry loop will be used to extend sodium corrosion and impurity chemistry studies to a pumped sodium system, to evaluate sodium sampling and impurity monitoring methods, and to provide a controlled well-characterized source of sodium samples for analytical development and other experimental uses.

Construction of the loop was completed in May 1968. A series of runs were made to provide component shakedown and to aid in the development of operating techniques. Extended runs were subsequently carried out to determine variations in oxygen meter readings during nominally steady-state operation and to establish base-line characteristics of the meters. This information is needed to assess the significance of meter responses during future experiments.

During these experiments it was noticed that the oxide meter emf varied cyclically during the

course of a day while the loop ran under nominally constant conditions; these changes were believed to be due to changes in ambient temperature around the oxide meter upper housing. By providing a more nearly constant ambient temperature at the top of the meter, the maximum daily variation in emf during nominally steady-state loop operation was reduced to ± 3 mV.

B. MINUSHKIN, L. EMMA, C. TIERNEY

ELECTROCHEMICAL TECHNIQUES FOR SODIUM CHEMISTRY

L. NEWMAN, J. WEEKS

The objective of this program is to develop electrochemical research tools for studying impurity behavior in Na, which may also be used to study and monitor impurities in high-temperature sodium systems.

Electrochemical Oxygen Activity Meter

The object of this program is to understand the basic electrochemistry of the oxygen meter in order to eliminate the various problems experienced with the meter and to extend its usefulness. These problems include the variation in calibration between meters, the sudden shifts and/or drift in meter calibration, thermal hysteresis, the finite life of the meter, its operating temperature limitations, and ambient temperature effects. All of these problems can be related to the behavior of one or more of the three structural regions in the meter, the electrolyte, the reference electrode, and the electrode-electrolyte interfaces.

Electrolyte. A series of direct-current four-point conductivity measurements were made on a section of a UNC oxygen meter tube to determine the ionic transference number of the electrolyte over the normal oxygen pressure range of the meter. Data were obtained over a range of oxygen pressures from air to very dry hydrogen at temperatures of 200° to 850°C. The four-point conductivity method avoids the complication and confusion that results from polarization at the current-carrying contacts.

The data obtained at three oxygen pressures, air, He containing 10^{-6} atm O_2 , and very dry hydrogen (equivalent to Na,Na₂O at 700°C), are shown in Figure 18, as a plot of the log of the resistance vs the reciprocal absolute temperature. The dry hydrogen and helium data are linear over

the full range of temperatures studied and are independent of the oxygen pressure. The air data show a break at 270°C. The activation energy calculated from the data, 27,200 kcal/mole, is in good agreement with the value reported by Bates of Pacific-Northwest Laboratory, 27,700 kcal/mole. Resistance measurements were also made on UNC oxygen meter tubes in the cell configurations

and

at temperatures from 150° to 550°C. The temperature dependence of the resistance in all three cases is in very good agreement with that obtained from four-point conductivity measurements.

It is concluded from the conductivity data that the predominant mechanism for conduction in the UNC oxygen meter electrolyte ($ThO_2 - 15 \text{ wt } \% Y_2O_3$) is ionic in the oxygen pressure range from air to 10^{-30} atm (equivalent to Na,Na₂O at

Figure 18. The resistance of $ThO_2-15 \text{ wt } \% Y_2O_3$ as a function of temperature and oxygen pressure.

700°C) at temperatures from 300° to 850°C. Work is in progress to extend the transference number measurements to oxygen pressures below those encountered in liquid sodium containing 1 ppm oxygen. The Si, SiO₂ system approximates the oxygen partial pressure expected at <1 ppm sodium in the temperature range of interest. Some preliminary emf vs temperature measurements on the cell

indicate that the electrolyte may have a transference number less than unity at temperatures above 500°C when in contact with sodium containing low (<1 ppm) concentrations of oxygen.

Reference Electrode. The behavior of the emf with temperature, its time response after temperature change, and the rate of recovery after being contaminated with air were studied for the cell

and for a UNC oxygen meter electrode in sodium saturated with sodium oxide, i.e., the cell,

The emf vs temperature data obtained with cell I operating in purified helium in the temperature range 350° to 850°C are in very good agreement with data reported by Markin et al. and by Horsley and Belford with the cell

The electrolyte ZrO₂-CaO has been shown to have a transference number >0.99 at oxygen pressures corresponding to the Cu, Cu₂O, Ni, NiO equilibria, i.e., 10⁻¹⁹ and 10⁻²⁹ atm, respectively, at 400°C. Therefore, the transference number for the ThO₂-15 wt % Y₂O₃ electrolyte-electrode interfaces in cell I was also near unity, confirming the conductivity measurements reported in the previous section. The response of cell I to temperature changes below 650°C was slow, however, requiring times in excess of 24 hr to reach a steady emf.

The emf vs temperature data obtained with the UNC oxygen meter electrode did not exhibit the expected behavior for cell II. The theoretical temperature coefficient (dE/dT) based on emf data for Cu, Cu₂O and free energy data for Na, Na₂O is -0.39 mV/°C. The measured temperature coefficient was +0.1 to 0.3 mV/°C between 250° and 320°C, essentially zero from 320° to 330°C, and

-0.3 to -0.5 mV/°C above 340°C. The time required to reach a steady emf after temperature changes was 48 to 72 hr at 250°C, 16 to 24 hr at 320°C (the recommended operating temperature), and several hours even at 400°C. These observations emphasize the desirability of operating the oxygen meter at a constant temperature, and, since the behavior is closer to theoretical above 340°C, suggest that a slightly higher operating temperature (such as 350°C) should be beneficial. Once contaminated with air, cell I did not recover at an appreciable rate at temperatures below 650°C. The UNC electrode showed no evidence of recovery at temperatures up to 500°C.

It is concluded from these observations that the transference number of the ThO₂-Y₂O₃ interfaces in cell I is unity at oxygen partial pressures as low as 10⁻²⁹ atm. It is also likely that the Cu, Cu₂O/ThO₂ - 15 wt % Y₂O₃ interface in the UNC oxygen meter under normal conditions is also near unity. However, the temperature response of cells I and II are slow even at 400°C and the cells are very susceptible to gas contamination. This work points out the limitations inherent in the use of solid metal-metal oxide reference electrodes at the relatively low temperatures recommended for the commercial meters.

Coulometry Using Solid Electrolyte Cells. The objective of this work is to determine if solid electrolyte cells can be used for coulometric addition or removal of oxygen to or from sodium, so that the technique can be used to study reactions and oxygen bearing species in sodium, to develop a method for calibrating an oxide meter electrode with controlled coulometric additions or subtractions of oxygen, and to study the nature of the electrochemical reactions occurring at the electrode-electrolyte interface.

Preliminary work was done with the cell

No net transfer of oxygen was observed in either direction at currents from 0.1 to 5 mA and temperatures to 500°C. It is probable that the applied voltage, although below the decomposition potential of ThO₂-Y₂O₃, shifted the electrolyte to a region in which its conduction is predominantly electronic.

Subsequent work was performed using the cell

$$\text{Pt, O}_2(1 \text{ atm}) \parallel \text{ThO}_2 - 15 \text{ wt } \% \text{ Y}_2\text{O}_3 \parallel \text{Na, Na}_2\text{O}_{\text{dis}}$$

Oxygen appeared to transfer from left to right of this cell. F. SALZANO, H. ISAACS, B. MINUSHKIN, G. KISSEL, W. KALINOWSKI, V. WILLIAMS

Electrochemical Carbon Activity Meter

The object of this effort is to develop an electrochemical method for measuring the chemical activity of carbon in liquid sodium using an operating principle similar to that used in the oxygen meter. The first step in the development of an electrochemical carbon meter was to find an electrolyte reversible to carbon that is compatible with sodium or with a suitable diffusion barrier placed between it and the sodium.

During 1968 an apparatus was built and two electrolytes tested (Li_2C_2 and CaC_2) in the following cells.

- (1) Graphite $\parallel$ Li_2C_2 $\parallel$ Zr,ZrC
- (2) Graphite $\parallel$ Li_2C_2 $\parallel$ Graphite
- (3) Graphite $\parallel$ CaC_2 $\parallel$ Graphite
- (4) Graphite $\parallel$ CaC_2 $\parallel$ Ca,CaC₂
- (5) Graphite $\parallel$ CaC_2 $\parallel$ Zr,ZrC

Li_2C_2 was found to be an unsuitable electrolyte because of the formation of a highly conducting film on the solid at temperatures above 300°C, the chemistry of which is not understood. The results of potential measurements as a function of temperature on cells (3), (4), and (5) indicate that CaC_2 may be a suitable electrolyte reversible to carbon. The emf's developed by cell (5) at temperatures from 250° to 400°C were within 10% of the expected theoretical values (−1.8 V). Above 450°C

the cell appears to deteriorate because of the reaction

so that cell (5) degenerates to cell (4). The emf at 500°C was −0.320 V, which is close to the expected theoretical emf of cell (4) and which is further evidence that CaC_2 is reversible to carbon.

Work has begun to determine whether the cell

can be used to measure the activity of carbon in sodium.

F. SALZANO, W. KALINOWSKI

ANALYTICAL DEVELOPMENT

L. NEWMAN

The purpose of this work continues to be the development of suitable sampling and analytical techniques in support of both the sodium corrosion and sodium chemistry programs. In addition, analytical service is provided to support all phases of the program.

Determination of Oxygen in Sodium

Further studies were carried out to elucidate the nature of the analytical blank associated with the amalgamation method for determining oxygen. During the previous year, a 5- μg oxygen blank contributed by the glass amalgamation vessel was isolated. Additional oxygen contamination must be taken into account when samples from stainless steel tubes are analyzed without prior extrusion. Several series of experiments showed that this blank is proportional to the external surface area of stainless steel and amounts to 1 to 2 μg oxygen per linear inch of 1/2-in.-o.d. tubing. The contribution appears to be caused by oxygen contamination of the external tube surface.

T. PRACH, W. CROCKETT

Determination of Oxygen Concentration in Sodium by Uranium Gettering

Uranium metal can be used to determine the oxygen concentration in sodium. Uranium acts as an efficient getter for oxygen in liquid sodium in the 400° to 500°C range. This was shown by immersing thin foils of uranium in sodium containing fixed amounts of oxygen for periods of one hour and noting the resultant weight gain. Adherent oxide deposits were obtained at 500°C with no apparent breakdown up to weight gains ap-

Figure 19. Variation of the rate of oxygen uptake by uranium with oxygen concentration.

proaching 4 mg/cm². The relation between the rate of oxygen uptake by the uranium and the oxygen concentration in the sodium at 500°C (Figure 19) showed that the rate of the reaction is linear. The rate was not influenced by temperature variations when the oxide was adherent, and was markedly increased by stirring. These observations and the high rates observed indicate that the rate is limited by mass transfer of oxygen to the uranium surface.

The uptake of oxygen (ΔW) by uranium may be expressed by the equation

$$\Delta W = W_o \{1 - \exp[(-kA/W_{Na})t]\}$$

where W_o is the weight of oxygen in a weight W_{Na} of sodium, A is the surface area of the uranium, t the time, and k the mass transfer coefficient for oxygen in sodium for a given geometry and flow velocity. This equation can be used to determine the oxygen concentration in the sodium and the mass transfer coefficient when the weight of oxygen is changed by gettering with uranium in two consecutive steps at equal time. Where the oxygen concentration is not significantly changed, the equation can be expanded, and the oxygen concentration is then linearly related to the weight gain of the uranium as observed in Figure 19.

H. ISAACS, W. BECKER, G. SPIRA

Analysis of Sodium for Trace Metallic Impurities

Because of the nature of the samples involved, there has been a continuing shift from emission spectrographic methods to the less sensitive but more precise technique of atomic absorption spectroscopy. Analyses for Cr, Ni, Cu, Ca, and Mg down to the 1-ppm level are now performed routinely by this method.

A Wurtz-type reaction has been adopted as a dissolution method for most samples to be analyzed for trace metals. In this method, *n*-butyl chloride is allowed to react with the samples, producing a precipitate of NaCl which contains the trace metal, along with rapidly vaporizable organic materials. The previously used methyl (or ethyl) alcohol procedure for dissolving Na samples suffers from the drawback of producing strong NaOH which tends to leach trace elements from the glass containers used.

R. DOERING, S. TASSINARI

Radiation Effects

Work in radiation effects during 1968 included studies of its effects on possible LMFBR fuel cladding materials and on plastic deformation of bcc metals.

Table 12

Comparison of Properties of Type 304 SS and Cobalt-Base Alloys
(All specimens irradiated at $<100^\circ\text{C}$ to 1.3×10^{20} , $E > 0.82$ MeV.)

Alloy	Test temperature, °C	Yield strength, psi	Tensile strength, psi	Total elongation, %
HA-25 (10% Ni, 20% Cr, 15% W)	25	139,000	142,000	15
	650	45,000	70,000	17
	750	35,000	38,000	9.2
	800	39,200	41,500	2.3
UMCO 51 (28% Cr, 20% Fe, 2% Cb)	25	120,000	146,500	20
	650	46,400	68,600	9
	750	38,700	46,600	7.5
	800	34,200	39,600	6.5
Type 304 SS ^a	25 ^b	81,500	105,000	58
	600	26,000	40,600	14
	650	19,200	29,800	7.5
	650	24,800	31,700	14
	700	23,000	23,900	10
	750	15,800	18,100	13
	800	10,500	11,700	6

^aData on material annealed from 1050°C.

^bStrain rate 2%/min; all other specimens strained at 0.2%/min.

EFFECTS OF IRRADIATION ON REACTOR MATERIALS

J. CHOW, R. JONES

The work on fuel cladding materials consists of two parts. One part is to develop an advance and backup material for stainless steels for the LMFBR. For this part, the cobalt-base alloys have been tested. The other part is to improve the postirradiation high-temperature ductility of stainless steels by alteration of microstructures.

Cobalt-Base Alloys

A number of commercial and experimental Co-base alloys have been tested for resistance to elevated temperature embrittlement after irradiation.

It was found that when these alloys are given the recommended heat treatment for high strength (solution treated from 1175°C), they are embrittled after irradiation in a manner similar to that of austenitic stainless steels and Ni-base alloys at temperatures above 650°C. However, these alloys are nevertheless potential cladding materials at 650°C where their ductilities are about equal to those of type 304 SS but their strengths are much higher. Table 12 compares the tensile properties of two commercial alloys (HA-25 and UMC0-51) with annealed type 304 SS after irradiation to 1.3×10^{20} ($E > 0.82$ MeV).

A program has been initiated to improve the postirradiation ductility at high temperatures of Co-base alloys. The approach is to add a small

Table 13
Effects of Irradiation on Cobalt-Base Alloys^a With Titanium
(All specimens tested at a strain rate of 0.2%/min.)

Alloy	Irradiation fluence ^b	Test temperature, °C	Yield strength, psi	Tensile strength, psi	Total elongation, %
605 0.09% Ti	0	750	31,200	33,000	57
	0	800	17,500	19,000	87
	1.3×10^{20}	650	80,000	95,000	29
	"	750	32,400	39,800	24
	"	800	24,400	26,200	67
606 0.2% Ti	0	25	116,000	179,000	28
	0	650	74,600	82,400	45
	0	750	31,700	33,400	52
	0	800	18,500	19,800	63
	1.3×10^{20}	650	81,200	97,500	20
607 0.46% Ti	"	750	41,500	42,600	22
	0	25	117,000	178,000	15
	0	650	72,300	84,500	34
	0	750	32,900	35,000	47
	0	800	20,700	22,300	71
608 0.64% Ti	1.3×10^{20}	650	80,500	94,800	23.5
	"	750	41,500	44,100	28
	0	25	126,000	160,500	7
	0	650	78,800	92,500	45
	0	750	29,300	32,100	58
	0	800	16,700	19,000	67
	1.3×10^{20}	650	79,700	94,800	22
	"	750	40,300	42,700	39
	"	800	26,400	28,000	71

^a21% Cr, 10% Ni, 5% W, 5% Mo, 8% Fe, Bal Co; cold-worked and recrystallized at 870°C for 16 hr prior to test or irradiation.

^b $E > 0.82$ MeV.

amount of titanium, which Weir and co-workers at Oak Ridge have found to be beneficial in several alloy systems, and to refine the grain structure by thermal-mechanical treatments which were effective in improving the ductility of Fe-Ni-Cr alloys (see below).

The effect of Ti addition is being studied in two base compositions: 21% Cr, 10% Ni, 5% W, 5% Mo, 8% Fe, bal Co and 22% Cr, 21.5% Ni, 14% W, 1.25% Fe, bal Co. Four alloys of each base composition have been made with Ti contents varying from 0.1 to 0.6%. The pre- and postirradiation tensile properties for four alloys with the first-named base composition are shown in Table 13. The data presented are for alloys that were cold-worked and recrystallized at 870°C for 16 hr; the alloys have a uniform grain structure, of the order of a few microns in size.

The results (Table 13) indicate the usual high strengths of the Co-base alloys at elevated temperature, and they show a much improved ductility over the materials in the solution-treated condition (see Table 12). Also, in the fine-grain condition, the ductility after irradiation increases significantly when the test temperature is increased

to 800°C, whereas previous results indicated lower ductility with increasing temperature. The results obtained to date indicate no appreciable change in properties with variation of Ti from 0.09 to 0.64%.

Improvement of High-Temperature Ductility of Fe-Ni-Cr Fuel Cladding Materials

The austenitic stainless steels, which are the current choice for fuel cladding for liquid-metal fast breeder reactors, exhibit a severe loss in ductility at elevated temperature after a moderate level of irradiation. The effort at BNL has been to improve this ductility by altering the microstructure of the materials.

The mode of failure in irradiated stainless steels is grain boundary tearing, in preference to slip deformation within the grains. The approach being studied to improve ductility is to alter the grain boundary structure by thermal mechanical treatment to refine the grain structure in commercial stainless steels by lowering the C + N content that segregates in the boundary, and by introducing interphase boundaries in Fe-Cr-Ni alloys.

Several schemes of thermal-mechanical treatments have been tried on types 304 and 316 com-

Table 14
Comparison of Irradiated^a Fe, Cr, and Ni Fuel Cladding Materials

Materials	Test temperature, °C	Yield strength, psi	Tensile strength, psi	Total elongation, %
Annealed 304 SS	650 ^b	22,000	30,700	11
	750	15,800	18,100	13
304 SS cold swaged 92%, annealed at 760°C	650 ^b	24,000	30,000	35
	750	11,800	12,900	27
316 SS cold swaged 87%, annealed at 760°C	650	27,800	34,600	39
	750	13,000	15,700	39
16% Cr, 9% Ni, low C + N iron alloy [(C + N) < 0.01%]	650	24,900	32,500	40
	750	15,700	19,200	32
38% Cr, 20% Fe, 42% Ni superplastic alloy recrystallized at 760°C	650 ^b	28,300	32,000	52.5
	750	25,800	27,600	24
38% Cr, 20% Fe, 42% Ni superplastic alloy recrystallized at 927°C	650	36,600	39,800	35
	750	14,000	15,300	77
38% Cr, 20% Fe, 42% Ni, superplastic alloy recrystallized at 1038°C	650	38,600	42,500	28
	750	14,100	15,100	150

^aAll specimens irradiated to a fluence of 1.3×10^{20} , $E > 0.82$ MeV. Strain rate, 0.2%/min.

^bAverage of 2 tests.

mercial stainless steels. It was found that heavily cold working the steels ($\approx 90\%$ reduction in area) at room temperature followed by low temperature (760°C) recrystallization effectively increased the postirradiation ductility at 650° and 750°C . This treatment provides materials with a grain diameter of 3 to $5\ \mu$ and a very finely distributed carbide phase; it completely obliterated the prior grain boundaries. It is believed that all these changes in structure aided in improving the ductility.

N. J. Grant and co-workers [*Iron Age* 67 (1956) and *Trans. ASM* 45, 105 (1953)] showed that the ductility and stress rupture strengths were both increased if the carbon plus nitrogen content of stainless steels is kept $<0.01\%$. From Professor Grant of MIT some of a 16% Cr–9% Ni extra low carbon plus nitrogen iron base alloy was obtained for tests. The recommended heat treatment for this material is water quenching from 1115°C . It was found that the strengths at 650° and 750°C are slightly higher than those of annealed type 304 SS, and the postirradiation ductilities are 3- to 4-fold greater than those for type 304 at these temperatures.

Hayden and co-workers at International Nickel Co. [*Trans. ASM* 60, 3 (1967)] show that Fe–Ni–Cr alloys over a wide range of composition can be treated to exhibit superplastic behavior at temperatures above 750°C . When treated to attain superplastic behavior, these alloys have a very fine-grained, two-phase structure. The higher Ni alloys are austenitic with a fine precipitate of ferrite, and the lower Ni alloys are ferritic with a fine precipitate of austenite. It occurs to us that the interphase boundaries may not be as susceptible to irradiation embrittlement at high temperature as the austenite–austenite boundaries. Several alloys were tested and it was found that irradiation does not destroy their superplastic behavior when deformed at 750°C , and that, at 650°C , these alloys exhibit high ductilities and high strength as compared with those of type 304 SS.

Table 14 compares and summarizes the tensile properties at 650° and 750°C of irradiated annealed type 304 SS with the properties obtained by the various methods of improving ductility that have been studied. This comparison shows that all three methods studied improved the ductility by 2- to 5-fold. Furthermore, the increases in ductility were obtained in most cases without any sacrifice in strength.

PLASTIC DEFORMATION OF IRRADIATED bcc METALS

Ferrovac E Iron and Niobium

During the last year, work has proceeded on studying the behavior and effects of point defects in bcc metals. In an earlier study it was found that a fast neutron dose of 10^{20} nvt ($E > 0.82\ \text{MeV}$) changed the rate-controlling slip process in Ferrovac E iron at temperatures below about 300°K . Therefore, a program was initiated in order to determine whether a somewhat smaller dose (10^{18} nvt) was sufficient to affect the controlling slip process in iron or whether there was a lower limit below which neutron irradiation did not affect the slip process.

Measurements of the thermal component of the flow stress, the activation energy for slip, and the activation volume for slip showed that below about 250°K the irradiation again changed the slip process. As in the case of the 10^{20} nvt specimens, the new mechanism was connected with the interaction of gliding dislocations with the tetragonal distortions that are introduced around small dislocation loops in the lattice. Above 250°K the irradiation does not seem to have a marked effect, and it appears that the slip mechanism is similar to that operating in unirradiated iron.

In addition to the above work, an attempt was made to determine the nature of the point defect(s) which migrate(s) during stage III recovery in cold-worked and neutron-irradiated niobium polycrystals that occurs between 100° to 200°C . By using a strain-aging technique in niobium, which has been prestrained to 6% in elongation, it was shown that both oxygen interstitials and self-interstitials migrate in this recovery stage. For the niobium, which has been irradiated to a fast neutron dose of 10^{18} nvt ($E > 1.45\ \text{MeV}$), a similar result was obtained. However, the studies indicated that the precise nature of the recovery was dependent on the initial configuration of the point defects. P. Soo

Tungsten

In the past year work has proceeded on the study of the marked temperature dependence of the critical resolved shear stress in tungsten crystals. When tungsten crystals are very carefully prepared – especially avoiding surface damage – temperature dependence of the critical resolved shear stress is markedly reduced. This clearly indicates the notch sensitivity of the material is contributing to the

temperature dependence of the critical resolved shear stress, rather than an inherent lattice resistance.

In this regard experiments are continuing in an attempt to freeze in kinks in zone-refined tungsten crystals. As reported in a previous report [BNL 50111 (T-494), Jan. 1968], no decrease of the flow stress has been observed with an increase in kink density, which is required according to the kink model of dislocation dynamics. J. GALLIGAN

The Effects of Fast-Neutron Irradiation on the Mechanical Properties of Iron

Iron Containing Fe_3C . A previously reported decrease in the concentration of finer Fe_3C particles in 0.03% C-Fe after irradiation to 2×10^{20} nvt was due not to the irradiation but to the prior heat treatment. No effect of this irradiation on optical or electron transmission structures of Fe_3C carbides was detected.

In unirradiated and 2×10^{18} nvt irradiated specimens of 0.11% C-Fe and 0.35% C-Fe, small plastic tensile strains at 298° K or at 77° K produced cracks in Fe_3C particles. At 77° K, these cracks initiated cleavage cracks in the ferrite. At 298° K, more strain caused voids to form at the cracks or beside uncracked carbides. The paths of ultimate failure connected such voids. No effect of irradiation on the fracture mechanism was detected.

Ferrovac E Iron. Raw data from earlier tensile tests (J.G.Y. CHOW, S.B. McRICKARD, AND D.H. GURINSKY, In *Radiation Damage in Solids*, Vol. 1, p. 277, IAEA, Vienna, 1962) on contoured specimens of Ferrovac E with grain diameters of 0.016, 0.031, and 0.11 mm showed that nearly all ductile specimens had upper yield points and yield drops that increased with decreasing temperature and with decreasing grain size. Upper yield stresses increased continuously with decreasing temperature, and, in the temperature range of ductile-to-brittle transitions, were equal to the apparent fracture stresses of brittle specimens. Below 150° K, irradiation to 2×10^{18} nvt increased the yield drops in the 0.016 and 0.031-mm grain sizes but not in the 0.11-mm grain size. Maximum yield drops then decreased with increasing fluence to 2×10^{20} nvt, while the lower yield stresses increased. Effects of fluence on the upper yield stresses were consistent with corresponding effects on the ductile-to-brittle transition temperature. These observations indicate that the observed radiation-induced ductile-to-brittle transitions were caused by the effects of irradiation and temperature on the upper yield

stress, i.e., on the stress necessary to actuate sources of dislocations or possibly of twins in the unstrained iron.

The magnitudes of reported discontinuities in yield stress and reduction of area at transitions were commensurate with those of yield drops in ductile specimens near the corresponding transitions. The reported discontinuous increases in yield stress at the transitions were observed because, in ductile specimens, the standard technique for determining yield stresses from contoured specimens obtains a stress slightly below the lower yield stress corresponding to lower limit of stress to move mobile dislocations in unstrained iron; but in brittle specimens the same technique obtains a stress slightly below the upper yield stress because fracture interrupts the deformation process just after the beginning of the yield drop. Results from several specimens that were ductile at temperatures below the reported transitions indicated that the minimum stress for moving mobile dislocations in irradiated unstrained iron increased continuously with decreasing temperature through and below the reported transition ranges.

Changes in the slopes of load-elongation curves at the base of the yield drop revealed changes in the limit of uniform strain before necking (i.e., in the strain-hardening exponent) which were not always detectable from the true stress-strain curves. Below 270° K, the exponent decreases with decreasing temperature and with increasing fluence up to 2×10^{20} . This behavior is consistent with known effects of irradiation on fracture toughness.

J. BRYNER

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.

EQUILIBRIUM IRREVERSIBILITY: EVIDENCE FROM SUPERCONDUCTIVITY FOR TWO TYPES OF HYSTERESIS

From a generalized treatment, hysteresis can be subdivided into two types which differ by conti-

nuity and discontinuity of the Gibbs free energy in the hysteretic domain. The condition that the Gibbs free energy is continuous in a hysteretic domain requires that different states in the domain have the same free energy. The existence of isothermal reversible paths peculiar to the hysteretic domain is associated with this type of hysteresis. Irreversibility, which arises as a result of equilibrium, occurs when intrinsic restraints exist for the number and interactions between the generalized forces and displacements which define the Gibbs function. The general concepts have been applied to properties of hysteretic superconductors to account for and determine the unique restrictions for new reversible processes that are created by the hysteretic state.

The data show that in fact, as well as in principle, the properties of hysteretic superconductors lie between two limiting types, one of which can be explained from equilibrium concepts. This type exhibits isothermal reversible paths whereas the other does not. The type exhibiting such reversibility retains fields of one polarity. The other type can retain fields of both polarities simultaneously. Magnetic stored energy releases and flux jumping occur in the type that retains fields of both polarities. Marked differences exist in the general features of the magnetization curves of the two types. The original demagnetized state can be regenerated by isothermal field cycles in the type exhibiting reversibility but not in the second type. The dissipative heat can be related to the hysteretic area in the first type but not in the second. The properties of the second type are considered in terms of pinning concepts. The data show that there are new interactions and field energies that are not accounted for in existing pinning models. Various aspects of the theory and data illustrating the new effects have been published (see Publication List).

EFFECT OF SURFACE ENERGIES ON THE SHIELDING AND FIELD-RETAINING PROPERTIES OF HOLLOW CYLINDERS OF TYPE I SUPERCONDUCTORS

The diamagnetic and field-retaining properties of thin-walled type I hollow cylinders can be changed by more than an order of magnitude through the introduction of surface strains. High-purity hollow cylinders of Pb and Sn in which the surface strains are minimal shield external fields of only a few percent of the critical field, H_c , and do

not retain appreciable fields in the void when an external field exceeding H_c is removed isothermally. The shielding and field-retaining properties are influenced by localized phenomena. The introduction of local surface strains increases the local shielding properties during the application of an external field, and leads to the retention of large axial field gradients in the void after the applied field is removed. Fields of both senses can be retained in the void simultaneously when cycles are performed involving both senses of the applied field. Experiments show spontaneous field enhancement when type I superconductors are cooled in applied fields. A number of unexpected reversibility relations are associated with these phenomena. The effects can be accounted for by including surface and interface energy terms in the thermodynamic state function of the superconductor. The data and an explanation of the results have been published (see Publication List).

D. SCHWEITZER

THE DYNAMIC RESPONSE OF SUPERCONDUCTORS

The dynamics of superconductors (their response to electric fields) is being studied theoretically. The simple form of mean field theory which has recently enjoyed favor is not adequate to obtain the response, i.e., the conductivity. Thus, the dynamic behavior of superconductors, in general, contrasts with the static response to a constant magnetic field. The latter case has been very satisfactorily explained starting from the hypothesis of Ginzburg and Landau that the free energy of a superconductor near a second-order phase transition may be expanded in powers of the order parameter and its gauge invariant spatial derivatives. The minimization of the free energy gives a differential equation for the order parameter from which the spatial form of the order parameter, the critical fields, the magnetization, etc., may be calculated in good agreement with experiment. It has been proposed that a gauge invariant time derivative be added to the differential equation from which the dynamics may then be calculated. This addition is not enough in general even for the most favorable case of alloys with short mean free paths. Other contributions to the response must also be included which do not arise directly from changes in the order parameter.

Usually an electric field is screened out of a superconductor, but there are three cases in which

the dynamic response may be measured for weak fields: (1) flux flow resistance, (2) microwave resistance, and (3) fluctuation resistance. New predictions for each of these three cases have been made. Currently we are investigating experimentally the third case most closely in the laboratory in collaboration with J. Crow, A. Bhatnagar, H. Fine, and M. Strongin. Measurements are being made of the resistance of aluminum films above the transition temperature. Analogously to the susceptibility of a magnet which diverges as its transition temperature is approached from above, in our experiments in addition to the normal state conductivity an extra conductivity is observed above the transition temperature due to statistical fluctuations of the normal state electrons into unstable superconducting states. Preliminary measurements are in substantial agreement with the new theory as to magnitude and to temperature and magnetic field dependence of the resistivity.

R. THOMPSON

NUCLEAR ORDERING AT LOW TEMPERATURES

An attempt to observe the ordering transition of the nuclear spin system of solid ^3He has been started. This experiment is made feasible by the availability of the compact 100-kG magnet constructed by W. Sampson in this laboratory. Our initial measurements were performed in the temperature range 0.040° to 0.200°K . In this relatively high temperature range our result is that the nuclear susceptibility follows a Curie-Weiss law, with ordering temperature magnitude, $|\theta|$, $< 0.005^\circ\text{K}$ for the largest stable molar volume, 24 cc/mole. The method used is that of simultaneous measurements of the nmr absorption of the ^3He spins and of a platinum powder nuclear spin thermometer. Two independently running Robinson circuits were used. Measurements were made for magnetic fields between 500 and 1000 G.

The result quoted above is in agreement with a large body of nuclear relaxation and thermodynamic data from which an ordering temperature of $\approx 0.002^\circ\text{K}$ has been inferred for the largest molar volume. Our aim is to observe the transition itself. Two means of cooling will be utilized simultaneously. These are nuclear adiabatic demagnetization of a matrix of copper wires and of the solid ^3He itself. Self-cooling of the ^3He is important below $\approx 0.005^\circ\text{K}$ because of decreasing heat transfer between copper and ^3He . More strin-

gent starting conditions than were initially anticipated are necessary. According to a recently published calculation of L. Goldstein, it is necessary to start below 0.010°K with a field of 100 kG. We have, therefore, made a new salt refrigerator of cerium magnesium nitrate designed to precool the experiment to 0.007°K . This refrigerator is located physically ≈ 40 cm above the high field magnet and is unaffected by it.

A technical problem of some difficulty concerns the remnant fields of the Nb_3Sn magnet. This magnet was wound from 0.090-in.-wide ribbon, is 4 in. long $\times$ 3 in. o.d. $\times$ 1 in. i.d., and produces a field of 105 kG at maximum current of 120 A. When the current is reduced to zero, large inhomogeneous fields remain trapped. The axial field is about +6500 G at the center and -6000 G at the coil end faces. These fields are at least three orders of magnitude too large for the nmr measurements. Cycling, reversing currents, and lowering the magnet away are unsatisfactory. A new compensation technique has been tried to alleviate this problem. Two short end coils are placed coaxially around the main magnet near the ends. These coils are self-energized by placing them in the persistent mode when the main winding is at a high current. As the main field is reduced, the end coils tend to keep a positive field at the ends. The field at the center can then be reduced by a suitable reverse current. At present, this technique is adequate as far as magnitude; however, the residual field gradients are still too large. It is hoped that this will be corrected by redistributing the end coil windings.

M. GARBER, W. KIRK,
E. OSGOOD

NEW MATERIALS AND SUPERCONDUCTORS

By deposition of metals onto cryogenic substrates, it has been possible to form unique structures that have never been studied before. In general the superconductivities of near monolayer sandwiches of different metals have been studied, and the conditions under which the maximum transition temperatures are attained in these systems were found. The increased transition temperatures in these systems can be convincingly explained by accounting for the effect of both internal and external surfaces on the lattice vibration frequencies of the metal in the layers.

Also studied was the nature of superconductivity in films down to about 10 Å thick that were de-

posited on insulating substrates. These films are extremely disordered, and the conduction mechanism in the "normal state" becomes more like a semiconductor, since the film resistance is found to increase with decreasing temperatures. In the regime where the conduction mechanism becomes nonmetallic, T_c is drastically reduced from the bulk value. It is possible that these films are almost completely disordered, even down to atomic distances.

A question which we intend to answer by diffraction work is the nature of the disordered state. Does disorder mean small randomly oriented crystallites? Or can there be disorder on an atomic level? The answer to these questions is crucial to the understanding of the increased superconductivity in the layered structures and also the decreased T_c in near monolayer films on dielectric substrates. The present work is also being extended to study transition metal films prepared with negligible gaseous impurities.

M. STRONGIN,
O. KAMMERER

Liquid State of Metals

A. PASKIN

Work on the liquid state of metals during 1968 included both experimental and theoretical investigations of resistivities, critical phenomena in partially miscible binary liquids, electromigration and diffusion in liquid alloys, and molecular dynamic studies in solids and liquids.

THE RESISTIVITY OF LIQUID MERCURY ALLOYS

A model for the resistivity of liquid Hg alloys has been developed. The experimentally observed large variation in resistivity of pure Hg with temperature, at constant pressure or with volume at constant temperature, may also be obtained from the conventional theory, provided the pseudopotential is assumed to be volume-dependent. A small linear dependence upon volume of the hard core radius of a simple form of pseudopotential [N.W. ASHCROFT, *Phys. Letters* **23**, 48 (1966)] gives satisfactory results.

The model developed here assumes that the net volume changes that occur on alloying Hg with most other metals may be associated with the Hg component alone, and that the volume-dependent pseudopotential derived from the properties of

Figure 20. Variation of resistivity with composition of liquid Hg-In alloys at room temperature.

pure Hg also applies to Hg when in the alloyed state.

The variation of resistivity with composition for the Hg-In system at room temperature is shown in Figure 20. The dotted curve represents the values calculated using a hard-sphere structure factor and a volume-dependent pseudopotential obtained as described above. In this calculation it is assumed that the component metals retain their normal valences. However, the experimental Hall coefficients of many Hg-based alloys indicate that in the free electron approximation the number of conduction electrons is larger than expected from the normal valences of the components. The resistivity calculated using these measured values is shown as the dashed curve in Figure 20. In both cases the initial rapid decrease in resistivity with increasing In concentration is closely reproduced.

This result indicates that the electrical resistivities of Hg and its alloys can be satisfactorily explained within the framework of the Faber-Ziman theory, provided that the Hg pseudopotential is assumed energy-dependent. The mechanism giving rise to this energy dependence has yet to be studied.

P. ADAMS

Figure 21. Temperature dependence of resistivity of a liquid Bi-Ga alloy.

CRITICAL PHENOMENA IN LIQUID BINARY ALLOYS

Over a certain range of temperature and composition, some binary systems, metallic or non-metallic, change from a single homogeneous liquid into two liquids of differing compositions, i.e., they exhibit a miscibility gap. It has been established for some time that in many binary organic liquids, concentration fluctuations occur in the immediate vicinity of the consolute temperature. This phenomenon has been observed by means of critical opalescence, specific heat, and acoustic absorption measurements. It is of interest as a critical point property and in the understanding of the second-order phase transition.

The existence (or otherwise) of concentration fluctuations in binary alloys is now under investigation here by means of electrical and acoustic measurements. It has been observed that significant deviations of the resistivity from the normal temperature dependence occur at up to 8°C above the consolute temperature. A typical curve of the variation of resistivity with temperature for a Bi-Ga alloy is shown in Figure 21. The results may be interpreted as indicating the existence of concentration fluctuations that give rise to an increase in the resistivity as the consolute temperature is approached. Other causes that could give rise to this effect are under investigation. P. ADAMS, S. FINK

ELECTROMIGRATION IN LIQUID ALLOYS

Electromigration in liquid alloys has been found to result primarily from "electron drag." A small

Figure 22. Drag coefficients of Ag and Au in polyvalent solvents plotted against the ratio of the experimental temperature to the melting temperature of the solvents.

fraction of the electrons' momentum is transferred to each ion species in proportion to its electron scattering cross section, σ . Using the electrical resistivity, ρ , of each species as a measure of σ , one should then expect the following relationship: $P = \rho_{\text{solute}} - \rho_{\text{solvent}}$, where P is the solute coefficient of electron drag. Indeed this relationship was found to hold quite well for many combinations of polyvalent metals, but it apparently breaks down for combinations of polyvalent and monovalent metals.

In Figure 22, values of P are plotted against the ratio of the experimental temperature to the absolute melting temperature for dilute alloys of Ag and Au in Hg, Tl, Pb, and Bi. Data points marked "S" were measured by Schwarz. Resistivity values in microhm-centimeters, measured at the respective melting points, are as follows: Ag, 17; Au, 31; Hg, 91; Tl, 73; Pb, 95; and Bi, 130. Based on the solute drag coefficients, Ag in Hg has an effective ρ of ≈ 40 , in Tl ≈ 60 , in Pb ≈ 80 , and in Bi ≈ 115 $\mu\Omega\text{-cm}$. Values of ρ_{eff} of Au are ≈ 55 in Hg, ≈ 80 in Tl, ≈ 100 in Pb, and ≈ 150 in Bi; in Pb and Bi the Au ions scatter electrons more strongly than Bi ions, and Au migrates to the anode.

Figure 23. Drag coefficients of a series of solutes in liquid Na vs the experimental temperature.

Figure 23 depicts the reverse case, that of polyvalent metals in a monovalent solvent. Values of P are plotted against the experimental temperature for alloys of Ag, Cd, In, Sn, and Sb in liquid Na. The solutes all migrate to the anode, as predicted by their relative resistivities; however, the magnitude of their electromigration parameters is about tenfold greater than would be predicted by the simple resistivity difference. Thus, these solutes have effective resistivities of several hundred $\mu\Omega\text{-cm}$ in Na. In the past this "abnormal" behavior in liquid Na had been attributed to the existence of compounds in the liquid. However, Ag, which does not form strong compounds with Na, also exhibits a relatively large drag coefficient, indicating increased electron scattering.

To further investigate this effect, a study was made with alloys of two monovalent metals, Na and K. The results are shown in Figure 24. In alloys containing 1 at. % K in Na, the K ions migrate to the anode, as expected. However, in alloys containing 1 at. % Na in K, the Na is found to migrate to the anode. The null point of this reversal occurs in alloys containing ≈ 34 at. % K, as shown in Figure 24. Since this is the composition of Na_2K , it had been thought that the existence of the compound in the liquid caused this peculiar behavior. However, Na_2K is a weak compound, dissociating before melting, and its presence in the liquid has not been detected by x-ray examinations.

In the alloys studied in which either of the species is monovalent, the solute ions exhibit greater than expected electron scattering. Probably the most significant difference between the monovalent and polyvalent metals is their electron densities, a property known to influence electron

Figure 24. Drag coefficients in NaK alloys vs the experimental temperature.

scattering. Thus, it is probable that introducing an ion into an environment of significantly differing electron density, either greater or less, increases its scattering cross section. Support for this proposal is seen in Figure 24. The alloy containing 34 at. % K shows no electromigration at temperatures below about 170°C , but some separation of the species is found at higher temperatures. The electron density of the alloy changes with temperature, leading to a change in the scattering properties of the species.

S. EPSTEIN, J. RUTHERFORD

DIFFUSION IN LIQUID SODIUM

Measurements were made of the diffusion coefficients, D , of a series of solutes, Ag, Cd, In, Sn, and Sb, in liquid Na. The results are shown in Figure 25, in which $\log D$ is plotted against the reciprocal of the absolute experimental temperature; in all cases the solute concentration is ≈ 1 at. %. The values of D are within the range of values usually found for diffusion in liquid alloys, and suggest no clustering in the liquid phase, as had been interpreted from diffusion studies of alkali metals in liquid Hg.

Sodium self-diffusion data, measured by Nachtrieb, are plotted on Figure 25 for comparison. It is

somewhat surprising that the rate of self-diffusion is about twice that for alloy diffusion, since the hard sphere radii of the solutes are considerably less than the radius of Na. However, the solute ions are about five times heavier than the Na ion, possibly accounting for their sluggishness, as the calculations of J. Dickey suggest; these are described in the next section. S. EPSTEIN, J. RUTHERFORD

MOLECULAR DYNAMIC STUDIES OF SOLIDS AND LIQUIDS

Computer programs have been developed that enable one to follow the classical motion of atoms arranged to simulate a liquid or solid. This motion can then be analyzed so as to give insight into a variety of problems. The atomic behavior in solids, at reasonable temperatures, depends on the interaction between atoms, which, for realistic potentials, contains an important anharmonic contribution. The usual method of analyzing the dynamics of a solid is to calculate the collective modes or phonons in the harmonic approximation. Since the forces are treated exactly in molecular dynamic calculations, the importance of anharmonicity can be investigated. Because of the anharmonicity, the phonons no longer form a set of independent collective coordinates, and the phonon frequencies and lifetimes depend on the volume

Figure 25. Diffusion coefficients of a series of solutes in liquid Na, plotted on a log scale vs the reciprocal of the experimental temperature.

and temperature of the solid. The dispersion curves and phonon frequency spectrum have been calculated as the temperature is increased at constant volume, and also as the solid expands.

The phonon spectrum of thin films affects critically their superconducting properties. Strongin and co-workers have observed increases in the transition temperature, T_c , of thin composite films consisting of alternating layers of dissimilar metals. It is estimated that the regions of the films that exhibit the greatest increase in T_c are within a few monolayers of the metal-vacuum or metal-metal interface. The phonon spectrum $f(\omega)$ of thin plate-like particles, a few atom layers thick, has been calculated. In Figure 26, $f(\omega)$ for the bulk sample (the upper curve) and for a particle of 166 atoms arranged in three layers (the lower curve) are compared. Corresponding to the longitudinal and transverse peaks of the bulk sample are the two right most peaks of the small particle. These are shifted slightly because of the slight softening of the interaction. In the small particle there are additional low frequency surface modes. By considering particles of varying size and thickness and by decomposing the velocity into its components, the first peak can be ascribed to edge modes and the second peak to membrane modes. The superconducting transition temperature depends on the moments of the frequency spectrum; these are shown in Table 15. It can be seen that, because of the very different shapes of the frequency spectra of the bulk solid and particle, the relevant moment $\langle \omega \rangle / \langle 1/\omega \rangle$ for the solid is almost twice that of the particle, and so is quantitatively large enough to explain the results of Strongin et al.

For many thermodynamic and transport properties of a liquid the hard sphere model is satisfactory. For example the diffusion coefficient of both metals and rare gas liquids is well described over a range of temperatures and pressures by the Enskog formula. However the available experimental evidence suggests that the Enskog formula fails for mixtures. The simplest example is a mixture of isotopes in which the size and forces between atoms are the same, and only the masses differ. The motion of 8 heavy (10 m) and 8 light (0.1 m) atoms in a matrix of about 700 atoms of mass m has been followed for about 4000 time steps corresponding to a time of $4.10 \cdot 10^{-12}$ sec. Figure 27 shows the average square displacement $\langle [r(t) - r(0)]^2 \rangle$ for the solvent and the two solutes. The diffusion constant is given by the asymptotic slope

Figure 26. Frequency distribution for an infinite crystal (upper curve) and a platelike particle 3 atom layers thick (lower curve). In reduced time units, the scale of ω is 1.33×10^2 and the scale of $f(\omega)$ is $2/\pi \times 1.33 \times 10^2$.

Table 15

Comparison of Moments of Frequency Spectrum
for the Crystal, Particle, and the Debye Model
for a 2- and 3-Dimensional System

(The units of frequency are those given in the caption
to Figure 26, and ω_D is the usual Debye frequency.)

	Crystal	Particle	Debye	
			3-Dimen- sional system	2-Dimen- sional system
$\langle \omega \rangle$	0.13	0.11	$0.75 \omega_D$	$0.67 \omega_D$
$\langle 1/\omega \rangle$	8.3	12.2	$1.5/\omega_D$	$2/\omega_D$
$\langle \omega^2 \rangle$	0.019	0.013	$0.6 \omega_D^2$	$0.5 \omega_D^2$
$\frac{\langle \omega \rangle}{\langle 1/\omega \rangle}$	0.016	0.009	$0.5 \omega_D^2$	$0.33 \omega_D^2$
$\frac{\langle \omega \rangle}{\langle 1/\omega \rangle \langle \omega^2 \rangle}$	0.85	0.66	0.83	0.67

Figure 27. Square displacement of solvent atoms (1), light atoms (2), and heavy atoms (3).

Figure 28. Velocity correlation of solvent atoms (1), light atoms (2), and heavy atoms (3).

of these curves, and also by the integral of the velocity correlation function which is shown in Figure 28. The coefficients of diffusion relative to the solvent are 0.6 and 1.0 for the heavy and light mass, respectively, whereas the values predicted by the Enskog model are 0.7 and 2.3, respectively. Within statistical uncertainty, the heavy mass agrees with the Enskog theory, whereas the light mass does not. The motion of the light mass is constrained by the surrounding solvent atoms, and although the velocity of a light atom is much

higher than that of a solvent atom, on the average, the diffusion of the light atom is governed by the realization of the matrix.

J. DICKEY

Metallography

O. KAMMERER

The majority of the metallography work during 1968 was performed in support of the several programs described above, where it is discussed. The following are a few observations of more than routine interest performed for those outside of the Metallurgy and Materials Science Division.

WELD QUALITY TESTS FOR AGS

A series of OFHC copper-to-carbon steel welds were examined to determine weld quality and migration of Fe into the Cu. The initial six specimens

contained numerous cracks and gas pockets. Subsequent specimens, however, exhibited good weld characteristics, with elimination of the included gases and cracking.

The electron-probe microanalyzer was utilized to determine the extent of Fe penetration. Particular emphasis was placed on the region within $20\ \mu$ of the Cu surface. The initial specimens had areas of heavy Fe concentration throughout the Cu matrix. The subsequent specimens, however, had Fe concentrations of $<0.1\%$ in the surface region examined.

A. CENDROWSKI, J. SADOFSKY

THIN FOIL EXAMINATION

Specimens of Hastelloy B sandwiched between Ag and CbSn were examined for W.B. Sampson of the magnet group. A typical foil is shown in Figure 29. The electron microprobe was utilized to determine the exact composition of all the layers and reacted areas.

J. HALFORD, J. SADOFSKY

Figure 29. Hastelloy B sandwich. 1000 $\times$.

Figure 30. Braze joint for AGS main ring magnet coil. 10 $\times$.

AGS MAIN RING MAGNET COILS

The braze joints for the AGS main ring magnet coil were evaluated. A series of sixteen specimens were examined. In most instances a lack of solder was noted in the ferrules of each joint. A typical condition is shown in Figure 30. A. CENDROWSKI

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Engineering Division

T.V. SHEEHAN

Heat Transfer Studies

J. CHEN, O. DWYER, M. HELFANT, P. HLAVAC, C. HSU,
S. KALISH, G. LINDAUER, G. STRICKLAND, W. YU

Heat transfer research in the Nuclear Engineering Department is concerned primarily with liquid-metal heat transfer. Both single-phase (liquid) problems and two-phase (boiling) problems are being investigated. The objectives of these investigations are (a) to obtain reliable experimental data and develop improved correlations for use in the design and safe operation of liquid-metal cooled reactors, and (b) to improve the understanding of the fundamental mechanisms of liquid-metal heat transfer and transport. In addition to this work, there is a small effort directed toward exploratory investigations of heat transfer problems in other fields. In the past year, this has included an experimental study of high-temperature gas heat transfer and an analytical study of cryogenic helium heat transfer. The Heat Transfer Research Group also continued to be responsible for the publication of the *High-Temperature Liquid-Metal Technology Review*.

Some results of various projects, obtained in this report period, are summarized below.

EFFECT OF ROD DISPLACEMENT ON HEAT TRANSFER TO MERCURY FLOWING IN-LINE THROUGH AN UNBAFFLED ROD BUNDLE

This, an experimental project, was completed during the year. It was described in some detail in last year's progress report, and a few preliminary results were given therein. The purpose of the study was to determine the effect of laterally displacing a rod in a staggered rod bundle on its heat transfer characteristics and on those of its six neighbors. The results are relevant to the design of sodium-cooled reactor cores. The test bundle consisted of thirteen 1/2-in.-diam rods arranged in an equilateral triangular pattern having a pitch : di-

ameter ratio of 1.75. The "rods" were special electrical heaters whose claddings were of different thicknesses and thermal conductivities. The experiments were carried out under a thermal boundary condition approaching that of uniform heat flux in all directions at the inner wall of the cladding. A representative portion of the bundle cross section is shown in Figure 1 where the central rod (location B) is in its symmetrical position. The central rod was displaced in two directions: $p \rightarrow q$ and $p \rightarrow r$.

It was found that displacement of a rod from its symmetrical position can result in a large reduction in its average heat transfer coefficient. This reduction increases exponentially with the amount of displacement. For a given direction and amount of displacement, the reduction is little affected by variations in cladding thickness and conductivity but is considerably affected by flow rate. Not only does the displaced rod suffer a reduction in its own average heat transfer coefficient, but so do those *toward* which it is displaced. At the same time, the average coefficients of the rods *from* which it is displaced remain about the same. Thus, the over-all average coefficient of the group of affected rods decreases when a single rod is displaced.

Figure 2 is a representative plot comparing the effects of three different claddings on the reduction of the rod-average heat transfer coefficient, $\bar{h}$, at a Peclet number of 2000. In the figure, h_o represents the heat transfer coefficient under symmetrical conditions, σ is the ratio of actual to maximum displacement, r_1 is the inner radius of the cladding, r_2 is the outer radius of the cladding, and k_w is the thermal conductivity of the mercury. Curves 1 and 3 show that a 4.2-fold variation in k_w had no effect upon $\bar{h}$, whereas comparisons between curves 1 and 2 and curves 3 and 4 show that a combination of a 5.2-fold variation in k_w and a 2.2-fold variation in cladding thickness had a small, though significant, effect. It is further seen that, for a given value of σ , the reduction in $\bar{h}$ is appreciably greater for a displacement in the $p \rightarrow r$ direction than one in the $p \rightarrow q$ direction. On the other hand, for a

Figure 1. Plan view of representative portion of test section showing spatial arrangement of rods and shell.

Figure 2. Effect of rod displacement on its average heat transfer coefficient illustrating the relative influences of cladding conductivity, cladding thickness, and displacement direction.

Figure 3. Effect of displacing the rod in location B on its own heat transfer coefficient and on that of the rod in location C showing the influences of displacement direction and variation in Peclet number. The rods were clad with stainless steel.

Figure 4. Effect of Peclet number on the circumferential variation of the local heat transfer coefficient for a rod in location B when it is moved halfway toward the rod in location C. Zero degrees represents the point of closest approach of the rod toward that in location C.

given absolute displacement, the reduction in $\bar{h}$ for a displacement in the $p \rightarrow q$ direction is more detrimental than that in the $p \rightarrow r$ direction.

Figure 3 summarizes the results obtained with the stainless steel-clad rods and shows the effects of relative displacement, displacement direction, and flow rate on the rod-average heat transfer coefficient. The Peclet number is defined as

$$Pe \equiv (D_e V_a \rho C_p) / k_f,$$

where D_e = equivalent diameter of bundle, V_a = average linear velocity of coolant, ρ = density of coolant, and C_p = specific heat of coolant. Thus, in the present study, variations in Pe are tantamount to variations in V_a . The k_w/k_f and $(r_2 - r_1)/r_2$ ratios pertaining to the curves in Figure 3 are the same as those for curves 2 and 4 in Figure 2. The large effect of Pe on the reduction in $\bar{h}$ for rods in loca-

tions B and C, caused by displacement of the rod in location C, is very evident. The Peclet numbers for most cores of advanced sodium-cooled fast-breeder designs fall in the 300 to 1200 range.

Finally, Figure 4 shows the effect of change in Peclet number on the circumferential variation of the local heat transfer coefficient, h , when the central rod is moved in the $p \rightarrow q$ direction. It is obvious that such large variations bring about corresponding variations in the surface temperature of the rod.

EFFECT OF SOLID-LIQUID INTERFACE CHARACTERISTICS ON HEAT TRANSFER WITH SODIUM

This study is an attempt to quantitatively correlate the characteristics of heating surfaces with

Figure 5. Sodium loop flow sheet.

Figure 6. Photograph of sodium loop taken during latter stage of construction.

their heat transfer behavior in sodium. Figure 5 shows a schematic flow sheet of the research facility which is scheduled for completion by the end of FY 69. The size of the facility may be judged from the photograph shown in Figure 6 taken in October. The test section is the last remaining major component to be installed in the loop circuit.

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 coefficients as a function of flow rate in the Peclet range 20 to 1000; (b) wall superheats ($t_w - t_{sat}$) for incipient boiling under conditions of natural circulation 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 for incipient boiling under conditions of forced convection as a function of pressure, heat flux, flow rate, and pressure-temperature history. All of this is relevant to the design and operation of sodium-cooled re-

actors. Data will be taken at temperatures up to 1600°F and pressures in the range 1 to 15 psia.

BOILING POTASSIUM STUDIES

In this report period the major effort in this project continued to be centered on the phenomenon of incipient-boiling superheat in alkali metals. Understanding of this phenomenon is important for the design and safe operation of liquid-metal-cooled fast reactors. The experimental work concentrated on two variables which are shown to strongly affect the magnitude of the superheat required to initiate incipient boiling, namely, (a) the preboiling deactivation (pressure vs temperature) history, and (b) the turbulent flow velocity at the time of boiling inception.

Additional results, showing the effect of varying deactivation conditions, were obtained from experimental measurements made in a forced-convection boiling-potassium loop. A description of the experimental method was given in the previous Annual Report [BNL 50082 (S-70)] and will therefore not be repeated here. Figure 7 shows a sample record of temperature and pressure conditions at the test section at the time of incipient boiling. It is seen that incipient boiling is clearly indicated by excursions of both temperature and pressure. For the run represented in Figure 7, the superheat measured at the moment of first vaporization was 81°F.

Figure 8 shows the effect of varying the subcooling to which the test heater is subjected during preboiling deactivation. Definitions of the nomenclature are:

T' = temperature at heater surface during deactivation,

P' = pressure at heater surface during deactivation,

T_s' = saturation temperature for test fluid at P' ,

P = pressure at heater surface at incipient boiling,

T = temperature at heater surface at incipient boiling,

T_s = saturation temperature for test fluid at P , and

ΔT_s = incipient-boiling superheat = $T - T_s$.

The data are compared with a semiempirical equation that has been proposed [J.C. CHEN, Incipient boiling superheats in liquid metals. *J. Heat Transfer Ser. C*, 90, 303-12 (1968); R. HOLTZ, ANL

Figure 7. Pressure and temperature behavior at the heated test section during incipient boiling of potassium.

7184, 1966]. Both the theoretical curve and the experimental data show that incipient-boiling superheats first rise rapidly, then level at some plateau as deactivation subcooling is increased. Figure 9 shows a composite plot of the experimentally measured superheats, compared with predicted superheats, as deactivation pressure and temperature are varied independently.

In the investigation of the velocity effect on incipient-boiling superheat, a different series of experiments with a new test section was performed with the boiling potassium loop. The experiments were designed to measure incipient-boiling superheats over a 15-fold range of velocity while maintaining constant deactivation T' , deactivation P' , boiling P , and heat flux. To our knowledge, this is the first experiment to so isolate the effect of velocity while holding T' and P' constant. The experiments were just completed and the data have not yet been reduced as of this writing. However, it can be reported that the qualitative results indicate a very strong effect of velocity, the superheat (ΔT_s) decreasing as velocity increased.

Figure 8. Effect of deactivation subcooling on incipient-boiling superheat. Experimental data compared with theory.

Figure 9. Composite effect of varying deactivation temperature and pressure on incipient-boiling superheat.

ANALYTICAL STUDY OF LAMINAR-FLOW THERMAL-ENTRY-REGION HEAT TRANSFER

An analytical study was carried out to determine the effect of axial conduction on thermal-entry-region heat transfer in laminar flow through concentric annuli. A theoretical solution was derived in closed form, and the first 20 eigenvalues and eigenfunctions were determined for a series of

Figure 10. Thermal-entry-region local Nusselt number for various Peclet numbers ($\sigma = 0.3$).

Figure 11. Variation of turbulent entrance effect with Prandtl number for concentric annulus.

Peclet numbers ranging from one to infinity. The series expansion coefficients were computed by solving a matrix equation for a system of simultaneous linear equations. The limiting case of $Pe = \infty$ corresponds to neglecting the axial conduction.

Fundamental temperature solutions were obtained for unilateral heat transfer in an annulus with uniform heat flux maintained at one of the annular walls and the opposite wall thermally insulated. The inner-to-outer radius ratio of the annulus, $\sigma (= r_1/r_2)$, was varied from 0.01 to 0.9. Figure 10 illustrates the variation of local Nusselt numbers, $[Nu^*]_1$ and $[Nu^*]_2$,[†] for $\sigma = 0.3$ and for various Peclet numbers. The effect of axial conduction is seen to be negligible for all Peclet numbers and axial distances of practical concern. For the given value of σ , $[Nu^*]_1$ can be observed to be always greater than the corresponding $[Nu^*]_2$. As σ is increased toward unity, i.e., the limiting case of parallel plates, the two Nusselt numbers become equal.

ANALYTICAL STUDY OF TURBULENT ENTRANCE-REGION HEAT TRANSFER TO LIQUID METALS

The objective of this project is to analyze the case of turbulent flow for (a) flow through concentric annuli and (b) in-line flow through rod bundles. Emphasis is placed on effect of axial variation in heat flux.

The analysis for flow in concentric annulus with heat input from the inner wall was completed in this report period. A rigorous solution, using eigenconstants evaluated by the method of Runge-Kutta, was obtained. One interesting result is that the thermal entrance effect was found to *not* simply increase with decreasing Prandtl numbers – as is usually assumed. Instead, for a given geometry and flow rate, the entrance effect was determined to first increase as Pr is reduced from $O[10]$ to $O[10^{-1}]$, then to decrease as Pr is further reduced below $O[10^{-1}]$. This is illustrated in Figure 11 for the case of an annulus with radius ratio of 1.5, for turbulent flow at a Reynolds number of 5×10^4 . The calculated ratio of local Nusselt number to fully developed Nusselt number, $Nu(x)/Nu(\infty)$, is plotted against Pr at three axial positions (x). A higher value for the ratio $Nu(x)/Nu(\infty)$ represents

[†] $[Nu^*]_i$ ($i = 1, 2$): local Nusselt number for the case where the inner or outer wall is uniformly heated.

a greater entrance effect. It is seen that the curves definitely show maxima in the region of $Pr \approx O[10^{-1}]$.

Extension of the solution to include cases of heat input from both walls of the annulus (at different heat fluxes) has also been completed but numerical results for sample cases have not yet been calculated.

DEVELOPMENT OF INDUCTION-HEATING FOR HIGH-FLUX LIQUID-METAL EXPERIMENTS

There currently is a need for methods to supply high-flux heating to alkali-metal experiments. Such heat sources are desired for liquid-metal heat transfer studies, reactor simulation experiments, liquid-metal corrosion studies, etc. The requirements for the desired heat source are the ability to operate at fluxes in the order of 10^6 Btu/(hr·ft²), the ability to heat test sections containing alkali metals at temperatures up to $\approx 1500^\circ\text{F}$, and reasonable reliability and cost. BNL has been investigating high-frequency (kilocycle range) induction heating as one possible answer for this need.

Because of the unique aspects of using induction heating in conjunction with high-temperature alkali-metal systems, a number of specific problems had to be overcome. Among other things, this has led to the first use of NaK as a coolant in the induction coil and the development of a resonant choke-coil to be applied in parallel with the induction coil.

In this report period, the first working trial of an induction-heated test section was performed in a pumped potassium loop at temperatures up to $\approx 1800^\circ\text{F}$. All aspects of the induction-heating system worked as well as, or better than, anticipated. In this first trial, the design heat flux of 250,000 Btu/(hr·ft²) (for this particular test section) was easily exceeded by 40%. The results show that, for future test sections of suitable geometries and materials, the induction-heating method can supply fluxes of 1 to 2×10^6 Btu/(hr·ft²).

DEVELOPMENT OF A PROBE FOR DETECTION AND MEASUREMENT OF VOIDS IN LIQUID METALS

A probe was developed for the detection of vapor or gaseous voids in liquid metals. With a sensing element of ≈ 0.5 mm diam, it is possible to obtain indications of point conditions. Probe response is of the order of 1 msec to a step change

Figure 12. Void probe response to air bubbling through mercury pool.

from liquid to void or vice versa. The probe is suitable for use in liquid metals at temperatures up to 1600°F .

The probe was tested in a bubbling air-mercury system. Figures 12a and 12b present sample recordings of the void probe signals as air was bubbled through a pool of Hg at two different flow rates. It is seen that the probe gives well defined signals of contact with the rising bubbles so that it is possible to quantitatively determine both the frequency of bubbles passing the point of measurement and the duration of time required for each bubble to pass this point. Figure 12c shows a typical trace over a period of time, τ . The shaded portions of the trace correspond to times when the sensing point of the probe is in bubble voids. Therefore, the void fraction, averaged over the period τ , can be calculated as:

$$\alpha(r, h) = \frac{t_1 + t_2 + t_3 + \dots}{\tau}$$

It is important that the sampling period, τ , be sufficiently long to obtain a statistically meaningful average.

This probe promises to resolve a heretofore unsatisfied need, namely, a means for fast-response detection and measurement of void occurrence and growth in high-temperature liquid-metal systems.

COMPUTATION OF PHYSICAL PROPERTIES OF HELIUM AT LOW TEMPERATURES

Low-temperature forced-convection helium cooling systems for superconducting magnets are currently being considered. The supercritical helium

Figure 13. Calculated helium viscosities at low temperatures and high pressures.

Figure 14. Calculated helium thermal conductivities at low temperatures and high pressures.

coolant in such systems will probably operate in the temperature range $4^{\circ}\text{K} \leq T \leq 8^{\circ}\text{K}$ and the pressure range $10 \text{ atm} \leq p \leq 30 \text{ atm}$. Since the transport properties, thermal conductivity and viscosity, are necessary to estimate convection heat transfer coefficients, and since they have not been experimentally determined for these conditions, computations were performed to calculate them theoretically.

The calculations are based on a kinetic theory of dense gases composed of rigid, spherical molecules proposed by Enskog [D. ENSKOG, Kinetic theory of thermal conduction, viscosity and self-diffusion in certain dense gases and liquids. *K. Svenska Vetenskapsakad. Handl.* 63, No. 4 (1922)]. Although only two-body collisions were considered, the dilute-gas kinetic theory was enlarged to encompass dense gas effects by taking the finite size of the molecules into account.

Dimensionless helium viscosities and thermal conductivities, μ/μ_0 and λ/λ_0 , are plotted in Figures 13 and 14, respectively. The zero subscript refers to the dilute gas property. Calculated thermal conductivities and viscosities were compared with experimental data at $\approx 4^{\circ}\text{K}$ and 20°K , and agreement between theory and experiment was found to be within 7%. The calculated viscosities should be valid over the entire range of temperatures and pressures studied, whereas the calculated thermal conductivities should be valid except in the immediate region of the critical point, where they are probably substantially higher.

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 BNL for incorporating fission products into phosphate 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 Pacific Northwest Laboratory (PNL).

Pilot plant studies at BNL over the past four years have provided basic information for the design and operation of the demonstration prototype plant which is being operated with high-level waste in the PNL fuel recycle hot cell. The major efforts over the past year were centered on demon-

strating pilot plant operability with new Purex flowsheets, including those derived from uranium burnup levels as high as 45,000 MWd/tonne. A number of extended pilot plant runs were made to establish operating ranges, particularly with respect to temperature and chemical composition of feed. During these runs, abnormal conditions were intentionally imposed to determine operational latitude for the evaporator and melter units. For example, attempts were made to flood the melter by rapidly adding several liters of evaporator concentrate. The long runs also served to provide operational experience for PNL personnel who are associated with the phosphate glass program. In two of these runs with PW-1 20,000 MWd/tonne waste, the steady-state throughput was found to be 1.9 and 2.1 ft³ glass/24 hr, respectively. The overall runs were made without any serious incidents, and it was established that either of the waste compositions used in these runs was acceptable for prototype operation.

It was determined that the airlift pot which feeds the melter and the specific gravity and weight-factor tubes were especially susceptible to plugging. For this reason, a great deal of attention was given to these areas during the extended runs. As a result, a new type of feed pot featuring a programmed feed splitter (similar to the system used to control feed to the BNL evaporator) was fabricated of glass and tested in the BNL pilot plant. With this unit, evaporator concentrate was lifted to the feed pot as shown in Figure 15. Although this system operated satisfactorily, it was recommended that the orifice of the original (PNL designed) feed pot be removed and a tapered plug valve be installed in its place. This device, which provided for varying the flow through the annulus, was tested in the BNL pilot plant and proved to be satisfactory. As a result, the feed pot in the PNL prototype was modified.

Another component which was modified during the past year was the platinum feeder for the melter. It has been the practice to prevent overheating of the solution flowing through the feeder by means of boiling water, under reflux, in a jacket around the central tube. Since viscosity becomes a limiting factor with continued evaporation and denitration, temperatures well above 100°C in the central tube would be desirable. Thus, a new solution feeder was designed and fabricated with an insulating annular zone between the cooling jacket and the central tube carrying the evaporator con-

Figure 15. Glass feed splitter.

centrate. This modification will permit transfer of the evaporator concentrate to the melter with little or no reduction in temperature and, accordingly, it will be possible to concentrate the solution to a greater extent.

Studies have been made on new types of Purex waste (PW-4 and PW-4m) having a low iron content and associated with 20,000 and 45,000 MWd/tonne U burnup, respectively. The evaporator solution boiling point, extent of denitration, volume reduction, and viscosity of the evaporator concentrate were first determined in laboratory-scale equipment, as well as glass forming temperatures and characteristics of the glass with a number of additions of sodium, phosphate, and iron. The composition of the feed solution for PW-4m was found to be essentially the same as that of PW-1 except for a reduced amount of nitric acid. A preliminary run was then made for 12 hr with a 5-hr concentration stage. The run was carried out without incident. The screw pump performed well when operating in the range of 300 to 350 rpm and fine control was achieved. During a shutdown period the pump plugged but it was indicated that plugging could have been prevented if the line had been flushed with dilute nitric acid.

PLATINUM AS A CONSTRUCTION MATERIAL FOR HIGH TEMPERATURE CRUCIBLES

During one run it was noted that the 8 × 24-in. cylindrical platinum crucible had become distorted by a slight flattening in one area of the wall. This occurred after ≈ 29,000 hr of intermittent service

Figure 16. Distorted crucible.

between 900° and 1200° C. Successive changes in the crucible wall were noted and carefully observed during the next 135 hr of operation, and the crucible was then removed for inspection. A photograph of the crucible (Figure 16) shows the extent of dimensional change. Examination of the platinum specimens from the crucible were particularly interesting because of the relatively long exposure under glass-forming conditions. Grain growth and other factors are being carefully observed and measurements are being made in an effort to determine the cause of the distortion of the crucible wall.

The crucible was examined by the manufacturers (Englehardt Industries), and their recommendations were obtained with respect to the repair of the distorted crucible and fabrication of a new one. As a result, it was decided that the crucible be retired and a new one fabricated with the following design changes: the 80-mil-wall thickness at the bottom of the crucible was extended upward 1 in. for a total of 7 in.; the next 6-in. section was increased in thickness from 0.040 to 0.060 in. and the upper section remained 0.040 in. thick. In addition, 4 stiffening rings, 0.060 in. thick and $\approx \frac{3}{8}$ in. wide, were welded to the outside. These changes were made to increase the strength of the vessel which seemed to have been inadequate under the existing conditions of support and vacuum operation.

NEW MELTER CONCEPT

In the operation of the PNL phosphate glass prototype, the capacity of the melter limits the over-all plant throughput to approximately a waste volume equivalent to one ton of uranium per day. The melter unit comprises a platinum crucible and an electrical resistance furnace wound with Kanthal Al wire. The furnace is operated at 1250° C although the wire manufacturer's specification is a maximum of 1300° C. Depending on the waste type being considered, the process requirement for volatilizing the water, nitric acid, and sulfuric acid and for forming a satisfactory glass is between 5 and 7 kW when the throughput of the plant is based on the reprocessing of one ton of uranium per day. It is apparent that the melter unit is operating very close to the calculated maximum.

To explore the possibility of improving melter throughput, new design concepts for the melter unit are being experimentally evaluated at BNL.

The approaches are (1) to increase the unit rate of heat input to the glass by the use of induction heating of the crucible and (2) to minimize the path length for the heat transfer inside the crucible. A new crucible, 8-in. diam with a 45° conical bottom, has been designed and fabricated; it is currently being tested for heating by means of a specially designed coil energized by a rf induction generator. The coil is a 45° copper cone to which one turn of a water-cooled electrical conductor has been soldered. The coil, designed to operate in the 450-kc range, is used in conjunction with a transformer to reduce the voltage and minimize arcing. The crucible is suspended by a Supermica 500 insulating ring and the two cones are $\approx \frac{1}{2}$ in. apart. In the first experiments, in which the heat flux distribution over the conical surface was studied, 10 and 20-kW output induction generators were used. The distribution was adjusted by machining the copper cone to slightly change the mating angle. It was apparent that the coupling with the 20-kW machine provides enough heat generation to keep the cone at $\approx 1000^\circ\text{C}$, but not enough to process significant amounts of glass. Since there are no more powerful 450-kc machines available at Brookhaven at the present time, a 50-kW motor-generator, 10-kc rf induction machine was used. With this machine and a makeshift coil of ≈ 10 turns, there was no difficulty in heating the crucible to 1200°C when the power level was $\approx 25\%$ of maximum. Based on these results, a new coil is being fabricated and experiments to measure the glass production rates are planned.

It has been observed in the laboratory that very short retention periods (of the order of a few seconds) is sufficient for conversion of the concentrate to glass. Based on this observation, the conical crucible will be fed at a number of points on the upper

inside surface, and it is expected that conversion to glass will take place as the concentrate flows by gravity over the surface of the cone.

MELTER OFF-GAS TREATMENT

Earlier work has shown that the melter off-gas condensate can be separated by distillation into its major components, nitric acid, sulfuric acid, and phosphoric acid. By distilling at modest vacuum in laboratory glass equipment, virtually all of the ruthenium remained with the phosphoric acid still-bottoms. Decontamination factors as high as 10^4 were achieved.

Experiments during the past year have been carried out with bench-scale equipment. A tantalum still-pot, 8 in. i.d. $\times$ 18 in. high, was provided with a 2-in.-i.d. $\times$ 24-in.-long tantalum fractionator tube. In addition, two water-cooled glass condensers, a Pyrex receiver, and a liquid nitrogen trapping system were installed in series with a vacuum pump. Batch distillations carried out at 9 to 28 mm Hg absolute pressure indicated that good separation of the various components can be achieved with this scale of equipment. However, ruthenium decontamination factors obtained in these runs were poorer than those in the earlier laboratory-scale experiments. On the basis of crude analyses by depth of color, the nitric acid fraction in each run indicated decontamination factors of $< 10^3$.

The use of a reductant to suppress ruthenium volatilization during distillation at atmospheric pressure was investigated as an alternative method. Two runs were made with the aid of Ru^{103} as a tracer in laboratory glass equipment using hypophosphorous acid as a reducing agent. Decontamination factors of 377 and 550 were achieved. How-

Table 1
Effect of SO_2 on Ruthenium Volatility During Distillation at Atmospheric Pressure^a

Run	Packing height, ^b in.	SO_2 feed rate, cc/min	Temperature range, $^\circ\text{C}$	Amount evaporated, %	Over-all decontamination factor
3	0	85	100-343	94.5	1.24×10^3
4	6	55	100-385	93.2	1.05×10^4
5	6	85	100-416	92.3	1.96×10^4

^a250 ml of PW-2 melter off-gas condensate used in each run.

^b $\frac{1}{4}$ -in. glass beads used as packing.

Table 2
Bench-Scale Melter Condensate Distillation Runs With SO₂^a

Run	SO ₂ flow rate, cc/min	Still-pot temperature range, °C	Distillation time, hr	Distillation rate, ml/hr	Volume distilled, %
B-1	230 ^b	100 to 345	3.69	812	96.3
B-2	120 ^c	100 to 340	3.00	790	79.0

^aThree liters of PW-2 melter condensate used in each run. No column packing used.

^bSO₂ fed in during heating-up period also. Total feed time, 4.58 hr.

^cSO₂ fed in during heating-up period also. Total feed time, 3.83 hr.

ever, because of possible dangerous chemical reactions with hypophosphorous acid and nitric acid, this work was discontinued. NO and NO₂ were also tried and were found to be unsatisfactory.

The use of SO₂ as a reducing agent was also investigated. Several distillation runs with Ru¹⁰³ tracer were made at atmospheric pressure in which SO₂ was introduced continuously by means of a dip tube in the still-pot; the results are shown in Table 1. Decontamination factors ranged between 1.24×10^3 and 1.96×10^4 depending on the SO₂ flow rate and amount of column packing used.

Two bench-scale distillations with SO₂ at atmospheric pressure were then made in the tantalum equipment described previously; the results are shown in Table 2. In run B-1 the distillate was colorless which indicated a low ruthenium volatilization ($DF > 10^3$). In run B-2, however, some color was observed with the last fraction of distillate which indicated a greater ruthenium volatilization ($DF < 10^3$). This can be accounted for by the reduced SO₂ flow rate in run B-2 compared with that of run B-1 (120 cc/min vs 230 cc/min).

KRYPTON AND XENON REMOVAL FROM OFF-GASES FROM FUEL REPROCESSING

Considerable progress was made in the development of a process for removing Kr and Xe from gas mixtures having low Kr and Xe concentrations, typically 100 ppm. Presumably, such concentrations would be found within a containment shell of a nuclear reactor as a result of reactor accident, or in off-gases from a typical fuel reprocessing operation.

As originally conceived, the process would combine the operations of liquefaction, fractional distillation, and inert fluidized bed reaction of O₂

with H₂ to concentrate the noble gases for final recovery by adsorption. The work done, however, indicates that simple stagewise adsorption, under the proper conditions, can provide a suitable product for storage or use. In any case, the gas to be treated would initially be passed through scrubbers to remove acid constituents and water vapor.

Gas mixtures were passed through beds of adsorbent at temperatures as low as -300°F . The beds were 10 in. long with diameters of $\frac{1}{2}$ and 1 in., and could be run singly or in series to give a variety of contact times. They were contained in the copper columns which were held in a cryostat cooled by a Norelco cryogenic unit. Temperatures

Figure 17. Schematic diagram of adsorption test apparatus.

were measured by thermocouples brazed to the columns and were controlled to $\pm 2^\circ\text{F}$ of the set point. A diagram of the test system is shown in Figure 17.

The test gas consisted primarily of mixtures of krypton (traced with Kr^{85}) and nitrogen, air, or helium. The last was used to simulate operation with pure Kr at low pressure, since He is not adsorbed at the temperatures used. This provided for a check of results against some figures for pure Kr published in the literature.

The Kr concentration in the gas was measured by monitoring the Kr^{85} in two scintillation counters, one placed before and one after the adsorbers in the flow scheme. By this means, the amount of Kr adsorbed at breakthrough, and at any degree of cleanup, could be measured. Since it developed that the breakthrough curves were symmetrical about the 50% point, the amount of gas passed through at that time could be used as a measure of the total capacity of the adsorbent at equilibrium, thus saving a considerable amount of time and material.

Two molecular sieves, types 5A and 13X, silica gel, and coconut charcoal were used as adsorbents at the start of the tests. It soon became obvious, however, that charcoal was better than any of the others by at least an order of magnitude, particularly in regard to total capacity, but also with respect to selectivity toward krypton. The effort was therefore concentrated on determining the characteristics of the adsorption of Kr on charcoal. Although the lower the temperature the better the results, a practical limit is foreseen above the point where oxygen in the process stream would be liquefied. This stems from the radiolytic

formation of ozone, which poses a hazard in the liquid state only. Since the liquefaction temperature of O_2 is -297°F at an O_2 pressure of 1 atm, a lower limit of operating temperature (-275°F) was chosen. This is also close to a practical operating maximum for economic industrial refrigeration methods.

The results of the work are indicated in Table 3, which shows the capacity of the charcoal and the degree of Kr enrichment obtained for several conditions of operation. In general, the equilibrium enrichment factors were remarkably independent of Kr concentration up to a level of 1000 ppm Kr, and were in the range of 80 to 100. The lower figure for the 100-ppm feed gas was probably due to channeling caused by high flow rate. The drop-off to the 65 to 70 level for the 4000-ppm feed gas is confirmed by the agreement among eight results for experiments in that region. Even this, however, would give a desorbed gas containing about 25% Kr by volume, and would be attainable in two stages of adsorption beginning with a 100-ppm gas mixture.

Adsorption figures for charcoal with pure Kr at low pressure, published by the Linde Company, indicate capacities on the order of 100 times those found for the dilute air mixtures of comparable partial Kr pressures. It was to check this point that the runs with He as diluent were made. The results are revealing. With a feed gas of 100 ppm Kr in air at -275°K , a breakthrough capacity of 0.268 cc Kr/g C was measured. Under the same conditions, but using He as the diluent, a breakthrough capacity of 26.4 cc Kr/g C was measured, which provides the factor of 100 called for by the Linde data.

Table 3
Adsorption of Krypton on Coconut Charcoal From an Air Carrier Stream at -275°F
(Air adsorbed = 200 cc/g C)

Feed gas concentration ppm Kr	Total mass velocity, lb/hr-ft ²	Contact time, sec	Kr adsorbed at breakthrough	cc/g C Equilibrium	Enrichment factor of desorbed gas	
					Breakthrough	Equilibrium
10	590	3.0	0.10	0.16	50	80
25	388	4.0	0.24	0.49	49	100
50	795	2.6	0.40	1.04	39	100
100	1220	3.3	0.57	1.25	29	63
1000	714	2.4	7.5	16.9	38	85
4000	630	3.5	33.3	55.6	42	70

Safety Studies

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The general purpose of this continuing research program is to provide a fundamental understanding of the chemical and physical behavior of the radioactive materials likely to be vaporized in the event of a reactor accident. This information is needed in making reactor hazard analyses and in designing engineered safeguard devices to be deployed in the event of an accident. It is also expected that the results of this research will lead to the development of inherent safeguard techniques which will limit the extent of release through natural processes rather than those which depend on the reliability of mechanically operational devices.

All of the research work carried out during the past year was done in support of the safety of sodium-cooled fast reactors. The current program comprises three major areas: (1) studies of the chemistry of fission product-sodium systems, (2) investigations of the formation, transport, and agglomeration of aerosols composed of plutonium oxide, uranium dioxide, and sodium, and (3) studies of the fission product chemical states and mechanisms and rates of release from fast reactor fuels.

SODIUM STUDIES

The information obtained in this phase of the program finds application in determining the

Figure 18. Excess free energies of mixing of NaI in sodium as a function of temperature. Standard state: liquid NaI at the temperature of interest.

distribution in the coolant, on surfaces, and in cold traps of the fission products either intentionally or accidentally released to the primary system. Furthermore, the results are useful for calculating the rate and extent of release from the primary system into the containment vessel in the event of an accident.

Analytical and experimental determinations of the thermodynamic properties of NaI, Cs, Rb, Sr, Ba, Te, and Sb solutions in sodium continued during the year. As a result of a controversy in the literature (W.P. KUNKEL ET AL., *LMFBR Fission Product Contamination and Control Studies - A Status Report*. AI-AEC-12687, June 30, 1968) regarding the activity coefficient of dilute solutions of sodium iodide in sodium below the NaI melting point (934°K), our earlier studies were extended to temperatures as low as 796°K. All of the data, including the earlier measurements at higher temperatures, are plotted in Figure 18. A partial molar heat and excess entropy of mixing of 15.9 kcal/mole and 6.8 eu, respectively, were obtained from the slope and intercept of the plot. These results confirm our earlier work.

Generally, only the limiting concentration region of infinite dilution is of interest, since the total quantity of fission products dissolved in the sodium coolant is usually very small. However, because of the potential buildup of fission products in the sodium thermal bond of high-burnup fuel elements, regions of higher concentration are also of practical interest. Therefore, our earlier thermodynamic calculations were extended to these higher concentration regions.

The partial molar excess free energies, entropies, and heats of mixing of sodium iodide-sodium solutions for salt concentrations up to 6 mole % were calculated. This was accomplished by using the experimental results for the dilute solutions together with a power series representation of free energy in terms of concentration. The calculations were performed by equating the total free energy along the tie lines of the phase diagram, and substituting the experimental partial molar excess free energy of mixing values, $\Delta \bar{F}^E$, into the power series expression. The results are given in Table 4.

Because of the relative high volatility of metallic cesium, as well as the long half-life (30 yr) and the relatively high fission yield of the 137 isotope, the thermodynamic properties of sodium-cesium solutions are of considerable interest. By employing the phase diagram, the activity of cesium and sodium is readily calculated by equating free en-

ergies along the tie lines between the pure component and the respective liquidus curve. The partial molar free energies of mixing, computed from these data, were corrected to a reference temperature by using published heat-of-mixing data [T. YOKOKAWA AND O. J. KLEPPA, Heats of mixing in binary-liquid-alkali-metal mixtures. *J. Chem. Phys.* **40**, 46-54 (1964)], which was recomputed using a power series method. The appropriate heat and partial molar excess entropy of mixing values are given in Table 5.

The rubidium-sodium phase diagram is very similar to that of the cesium-sodium system, showing a simple eutectic at 75.5 mole % Rb. Consequently, a method similar to that used for the cesium-sodium system was also employed here. The thermodynamic properties deduced for this system are given in Table 6.

The analytical method used to evaluate the sodium solution of cesium and rubidium was employed to calculate the $\Delta\bar{F}^E$ values for the Ba-Na

Table 4

Thermodynamic Properties of NaI-Na Solutions

x_{NaI}	$\Delta\bar{H}_{\text{NaI}}$, kcal/mole	$\Delta\bar{S}_{\text{NaI}}^E$, eu
0	15.95	6.8
0.001	15.65	6.6
0.002	15.45	6.5
0.005	15.00	6.2
0.01	14.35	5.8
0.02	13.32	5.2
0.04	11.24	4.0
0.06	9.76	3.2

Table 5

Partial Molar Quantities for Liquid Na-Cs Alloys

x_{Na}	$\Delta\bar{H}_{\text{Na}}$, cal/mole	$\Delta\bar{S}_{\text{Na}}^E$, eu	$\Delta\bar{H}_{\text{Cs}}$, cal/mole	$\Delta\bar{S}_{\text{Cs}}^E$, eu
0.0	518	-1.24	0	0
0.1	515	-0.67	0.3	-0.03
0.2	498	-0.29	3.4	-0.09
0.3	464	-0.11	15	-0.15
0.4	411	-0.03	44	-0.20
0.5	340	0.00	103	-0.22
0.6	253	-0.02	209	-0.20
0.7	191	-0.01	325	-0.23
0.8	126	0.02	525	-0.30
0.9	48	0.02	987	-0.26
1.0	0	0	2019	0.15

Table 6

Partial Molar Quantities for Liquid Na-Rb Alloys

x_{Na}	$\Delta\bar{H}_{\text{Na}}$, cal/mole	$\Delta\bar{S}_{\text{Na}}^E$, eu	$\Delta\bar{H}_{\text{Rb}}$, cal/mole	$\Delta\bar{S}_{\text{Rb}}^E$, eu
0.0	843	-0.37	0	0.
0.1	781	0.15	4	-0.02
0.2	699	0.36	18	-0.06
0.3	602	0.37	51	-0.06
0.4	494	0.27	110	0.00
0.5	381	0.14	203	0.10
0.6	290	0.08	315	0.17
0.7	191	0.03	500	0.27
0.8	98	0.00	784	0.37
0.9	27	0.00	1188	0.39
1.0	0	0.00	1722	0.19

Table 7

Partial Molar Quantities for Liquid Na-Ba Alloys

x_{Na}	$\Delta\bar{F}_{\text{Na}}^E$, cal/mole	$\Delta\bar{F}_{\text{Ba}}^E$, cal/mole
0.0	1010	≈ 0
0.1	1010	≈ 0
0.2	1010	≈ 0
0.3	1010	≈ 0
0.4	1010	≈ 0
0.5	1010	≈ 0
0.6	1000	10
0.7	915	85
0.8	600	275
0.9	120	615
1.0	0	1700

Table 8

Partial Molar Quantities for Liquid Na-Sb Alloys

x_{Na}	$\Delta\bar{H}_{\text{Na}}$, cal/mole	$\Delta\bar{S}_{\text{Na}}^E$, eu	$\Delta\bar{H}_{\text{Sb}}$, cal/mole	$\Delta\bar{S}_{\text{Sb}}^E$, eu
0.0	-10,845	-11.1	0	0
0.1	-8,790	-8.99	108	-0.11
0.2	-6,945	-7.10	434	-0.44
0.3	-5,310	-5.44	976	-1.00
0.4	-3,905	-4.00	1,736	-1.78
0.5	-2,710	-2.78	2,710	-2.78
0.6	-1,736	-1.78	3,905	-4.00
0.7	-976	-1.00	5,310	-5.44
0.8	-434	-0.44	6,945	-7.10
0.9	-108	-0.11	8,790	-8.99
1.0	0	0	-10,845	-11.1

Table 9

Partial Molar Quantities for Liquid Na-Te Alloys

x_{Na}	$\Delta\bar{F}_{\text{Na}}^E$, cal/mole	$\Delta\bar{F}_{\text{Te}}^E$, cal/mole
0.1	-3475	-70
0.2	-2648	-214
0.3	-1989	-433
0.4	-1444	-727
0.5	-994	-1095
0.6	-632	-1537
0.7	-354	-2053
0.8	-156	-2645
0.9	-39	-3310
1.0	0	-4050

Figure 19. A schematic diagram of the apparatus employed in the fission-product vaporization studies.

system as well. Since no heat of mixing values exist, the solutions were assumed to be regular, i.e., the partial molar excess entropy of mixing was taken to be zero. The $\Delta \bar{F}^E$ values for barium and sodium are given in Table 7.

Regarding the elements of groups V and VI, antimony and tellurium are the fission products of major importance. Partial molar excess free energy values were calculated and are given in Tables 8 and 9.

The thermodynamic properties have a bearing on the transport of the fission products, their partial pressure, and extent of vaporization from solution. The partial pressure, P_i , of a solute in solution is given by the equation

$$P_i = P_i^0 \gamma_i x_i, \quad (1)$$

where P_i^0 is the vapor pressure of the pure substance and γ_i and x_i are the respective activity coefficient and mole fraction in solution. Since

$$\Delta \bar{F}_i^E = RT \ln \gamma_i, \quad (2)$$

these values of $\Delta \bar{F}_i^E$, together with vapor pressure data, lead directly to the fission product partial pressures.

The rate of nonequilibrium vaporization of fission products is usually governed by diffusional

resistances. Although the release of a species from a liquid solution into the vapor phase is often largely governed by a controlling resistance in one phase or the other, in some cases diffusion in both phases is important. During the year, experimental and analytical studies of fission product vaporization from molten sodium into a flowing gas stream were completed.

It was found that the vaporization of cesium from sodium solutions into an inert gas stream could be adequately described by an analytical model taking into account resistances in both the liquid and gas phases and assuming equilibrium to exist at the interface.

Solving the appropriate differential equations leads to the following expression for the fractional release

$$F = 1 - \sum_{n=1}^{\infty} \frac{2L^2 \exp(-\beta_n^2 Dt/l^2)}{\beta_n^2 (\beta_n^2 + L^2 + L)} \quad (3)$$

where the β_n 's are the positive roots of

$$\beta \tan \beta = L, \quad (4)$$

$$L = l\alpha/D, \quad (5)$$

and

$$\alpha = (D_v/b) (P^0 \gamma / \rho RT), \quad (6)$$

Figure 20. Effect of molecular weight of carrier gas on the vaporization rate of cesium from liquid sodium.

and l is the liquid depth, b the gaseous diffusion path, ρ the molar density of sodium, D the liquid-phase diffusivity of cesium in sodium, and t the release time.

In principle, the fraction of cesium released during a given period may be calculated from this equation provided that all constants are known. For cesium release from sodium, the activity coefficient may be obtained from the $\Delta \bar{F}^E$ values given in Table 5, while the gas-phase diffusivity may be estimated using standard methods (J.O. HIRSCHFELDER, C.F. CURTISS, AND R.B. BIRD, *Molecular Theory of Gases and Liquids*, p. 539, John Wiley, New York, 1964). However, since liquid-phase diffusivities can only be estimated to the nearest order of magnitude, we chose to evaluate the constants D and α from two sets of experimental release data and used these parameters to deduce release rates under other conditions.

The release of cesium from liquid sodium into an inert gas stream was studied experimentally. A schematic of the apparatus is shown in Figure 19. Radioactive Cs^{137} was dissolved in sodium to form an alloy with a very low cesium concentration. To carry out a transport experiment, the resulting alloy was melted in a crucible of known dimensions to form a liquid phase of known depth and a well defined gas path above the liquid. The

Figure 21. A summary of the results from cesium vaporization experiments carried out at 730°K in flowing helium. The close agreement between the predicted release (dashed lines) and the experimental results (open triangles) is clearly shown.

crucible was heated to 730°K in an inert gas stream flowing at 300 cc/min. The rate of cesium release was monitored continuously with the scintillation counter.

Both the liquid depth and the molecular weight of the carrier gas were found to affect the release rate as predicted by Eq. (3). Figure 20 shows the results of two experiments, one made in argon and the other in helium. All other conditions were identical in the two experiments. It is seen that the release rate into helium was faster than that into argon, an expected result, since gas-phase diffusivities are inversely proportional to the square root of the reduced mass for the components of the system. Taking the results in argon as a basis, the release in helium should follow the dashed line if only a gas-phase resistance were operational. The fact that the two release curves show some separation but not enough to account solely for gas-phase diffusion indicates that the release is actually governed by mass transfer resistances in both phases.

Two helium experiments were used to evaluate D and α . These two runs were made with gas layers of 0.9 and 0.8 cm and liquid depths of 0.5

and 1.2 cm, respectively, and are shown as lines (B) and (D) in Figure 21. The diffusivity evaluated by this method is 8.1×10^{-5} cm²/sec compared to estimates ranging from 7×10^{-5} to 11×10^{-5} cm²/sec. It is evident that the procedure used to evaluate D from the experimental data does not simply result in the evaluation of an adjustable parameter, but gives quite a reasonable estimation of the liquid phase diffusivity.

With the evaluated α 's, D , and Eq. (3), the fractional cesium release was computed as a function of time for two other cases with liquid depths of 1.0 and 1.2 cm, and gas depths of 1.5 and 0.2 cm, respectively. The predicted releases are shown by the dashed lines (A) and (C), Figure 21. Experiments were then carried out with these geometric parameters. The experimental results, shown as open triangles, agree very well with the theoretical lines. It is concluded that Eq. (3) is valid for predicting the time dependence of fission product release from sodium.

The analytical model described above makes the assumption that the liquid phase is completely stagnant. This may be true in an ideal laboratory experiment where a small sample can be kept isothermal at a specified temperature. In large-scale systems where nonisothermal conditions exist, convection will result in greater release than that expected with molecular diffusion alone. Therefore, in making reactor safety analyses, it is desirable to be able to estimate the maximum release under the given conditions.

In considering the case of maximum release, it is apparent that complete mixing in the liquid phase will lead to a greater release rate than for a case where diffusion operates in two phases. Therefore, consider the case where both the solvent (Na) and solute (fission product) diffuse through a gas layer of constant thickness b . It follows from the solution to Fick's law with appropriate boundary conditions that

$$\ln(1 - F_1) = -(D_{v1}P_1/RTb\rho)(t/l) \quad (7)$$

and

$$\ln(1 - F_2) = -(D_{v2}P_2\gamma_2/RTb\rho)(t/l), \quad (8)$$

where subscripts 1 and 2 refer to solvent and solute, respectively. Dividing Eq. (8) by Eq. (7), one obtains

$$\frac{\ln(1 - F_2)}{\ln(1 - F_1)} = (P_2^0\gamma_2/P_1^0) (D_{v2}/D_{v1}) = A\phi \quad (9)$$

or

$$F_2 = 1 - (1 - F_1)^{A\phi}, \quad (10)$$

where

$$A = P_2^0\gamma_2/P_1^0, \quad (11)$$

$$\phi = D_{v2}/D_{v1}. \quad (12)$$

Eq. (10) reduces to the familiar Rayleigh equation for equilibrium vaporization when the ratio of the gas-phase diffusivities, ϕ , is unity. Since gas-phase diffusivity is inversely proportional to the square root of the reduced mass of the system, in the case of fission product-sodium systems the above diffusivity ratio is less than unity. Therefore, it is concluded that the Rayleigh equation represents an upper limit for the fractional fission-product release as a function of the fraction of sodium vaporized. The latter quantity may often be estimated by making a heat balance for the system under consideration. It is also obvious that appropriate $\Delta\bar{F}^E$ values are required in calculating the maximum extent of fission product release.

AEROSOL STUDIES

A consideration of the potential formation and transport of radioactive aerosols under conditions likely to exist in the event of a fast reactor accident is important both in the design of engineered safeguard devices and in the siting of reactors. Because of the health hazard associated with plutonium, it is important to understand the behavior of vaporized plutonium oxide. The lack of data on the behavior of vaporized PuO₂, PuO₂-UO₂, and PuO₂-sodium aerosols prompted us to undertake a long-range program to study these systems.

Experiments were carried out by vaporizing fuel and sodium with the use of resistance heaters. Gas flow or fans were employed to initially distribute the vaporized material in settling chambers. Since the primary objective of these studies is an investigation of the quantity of plutonium oxide remaining airborne, emphasis was placed on sampling the mass concentration and size distribution of the airborne particles as a function of time. This was accomplished by using thermal precipitators.

Several settling chambers, ranging from 0.4 to 1.0 m in height, were employed during the course of these experiments. Because of the health hazard associated with plutonium, all components of the apparatus were enclosed within the glove boxes

Figure 22. Alpha glove boxes used in plutonium fuel-sodium aerosol experiments. The man in the foreground is measuring the temperature of a plutonium oxide fuel being vaporized into an aerosol chamber within the glove box. The other man is controlling the furnace temperature via a rhyostat located under the glove box supports. After generation, the aerosol is flowed into the aerosol chamber at the far right, and is then sampled periodically. The size distribution of the aerosol samples is determined with an electron microscope.

The results from all experiments showed that the airborne plutonium oxide mass concentration initially dropped very rapidly, leveling off to a shown in Figure 22. These enclosures severely restricted the maximum size of the settling chamber that could be employed in these studies and necessitated the use of chambers that could be readily removed from the glove box and replaced. Therefore, larger chambers (1 and 0.75 m^3) were constructed of antistatic polyethylene film.

much slower rate of decrease after the first one-half to two-hour period. Usually, several days of settling time were required before the mass concentration dropped below 10^{-7} g/m^3 , the limit of detection in these experiments. All of the experiments showed that the aerosol settling rate was independent of the mass concentration within the range studied, i.e., 0.03 to 2.0 g/m^3 . It should be noted, however, that the aerosol generation rate was essentially the same in all experiments so that the mass concentration in the region of original nucleation may not have differed appreciably between runs. In these experiments, the reduction in airborne plutonium concentration was mainly due to settling, while plateout on walls generally accounted for only 10 to 15% of the total material.

Airborne particles are known to settle according to Stokes equation for Reynolds numbers below 0.1. The suspended particles also undergo

Brownian motion and agglomerate upon colliding. However, because of the relatively large different time scales in which the two processes operate, it is often possible to use simplified equations to account for particle settling and agglomeration in a semiquantitative manner. That is, initially agglomeration is very rapid while settling is relatively unimportant; for intermediate times of several minutes to several hours, settling is the dominant process and relatively little agglomeration takes place.

Following Sinclair (D. SINCLAIR, *Stability of Aerosols and Behavior of Aerosol Particles*, Chap. 5 in *Handbook on Aerosols*. U.S. Office of Scientific Research and Development, National Defense Research Committee, Washington, D.C., 1950) an equation was obtained which expresses the fractional change in airborne mass concentration, f , as a function of time, t :

$$f = \exp[-3.0 \times 10^5 (\rho d_8^2 / h) t]. \quad (13)$$

Here, h is the height of the enclosure in centimeters, ρ the particle density in g/cc, and t in seconds. The use of d_8 is necessary in order to account for the distribution of particle sizes. The diameter d_8 is given by

$$\log d_8^2 = 2 \log d_g + 18.424 \log^2 \sigma_g, \quad (14)$$

where d_g is the count mean diameter of the particles and σ_g the standard deviation of the size distribution.

A summary of the results from all pure PuO_2 and mixed PuO_2 - UO_2 aerosols is shown in Figure 23. Within experimental scatter, all of the PuO_2 data obtained to date can be represented by a single semilog plot of the fraction of PuO_2 remaining airborne as a function of t/h . The deviation from a straight line after a decrease of approximately one and a half orders of magnitude is undoubtedly due to a decrease in the product ρd_8^2 with time. Although the particles are growing with time, they are forming chain-like "fluffy" agglomerates whose density is much less than theoretical. Particle densities ranging from 4 to $< 1/2$ g/cm³ were experimentally observed after several hours of agglomeration.

Preliminary work indicates that the time dependence of UO_2 and mixed PuO_2 - UO_2 aerosol mass concentrations is somewhat different from that of pure PuO_2 . This difference is also shown

Figure 23. Behavior of PuO_2 and mixed PuO_2 - UO_2 aerosols.

Figure 24. Behavior of mixed PuO_2 -Na oxide aerosols.

in Figure 23 for the case of a 20 wt% PuO_2 -80 wt% UO_2 aerosol. The UO_2 and PuO_2 - UO_2 aerosols settle more rapidly, probably because of a larger over-all ρd_s^2 . It is not too surprising to expect UO_2 and PuO_2 aerosols to differ somewhat in behavior, since the vapor pressure relationships for these two oxides are considerably different, and they vaporize by different processes.

A conservative estimate of the product ρd_s^2 can be obtained from the slope of the dotted straight line shown in Figure 23. This value should be adequate for estimating the first one to two orders of magnitude drop in aerosol concentration. It is worthwhile noting that the product of the theoretical density and d_s^2 calculated from experimental d_g and σ_g values is in good agreement with that obtained from the figure.

The presence of sodium has some effect on the PuO_2 aerosol mass concentration behavior as seen in Figure 24. For sodium-to- PuO_2 ratios of 1, the long-time behavior of the aerosol is very much like that without sodium. However, with larger sodium-to- PuO_2 ratios, the experimental results indicate that the aerosol remains airborne for a much longer period of time. This observation is not unexpected. Since the densities of both sodium and its oxide are quite low compared with PuO_2 , the composite agglomerates, although larger in size, have a smaller density than the agglomerates of pure PuO_2 aerosols. This leads to a smaller value of ρd_s^2 and a more persistent aerosol.

RELEASE OF FISSION PRODUCTS FROM FAST REACTOR FUELS

This phase of the program was initiated to study the factors governing the chemical states of the fission products released from fast reactor fuels. Initially, studies will be done using PuO_2 and PuO_2 - UO_2 fuels with low to moderate burnup levels, with an extension of the work to higher burnup levels and higher fission product concentrations later.

A thermochromatographic apparatus is currently being constructed inside a large alpha-gamma cell. This facility will be used to separate the released fission products in a manner similar to that done with uranium fuels in the past. The collected species will then be analyzed using Knudsen cell vaporization techniques, possibly coupled with mass spectrometry. Construction of the facility is scheduled for completion during FY 1969.

Engineering Assistance Group

The Engineering Assistance Group is a service organization supporting departmental research programs. About 25 persons are involved in engineering, design, and construction of experimental equipment. The group also contributes to ANS and ASME committees, the *High-Temperature Liquid-Metal Technology Review* and the review of RDT specifications.

For the Experimental Reactor Physics Division, the group furnished engineering, design, and to some extent fabrication management for (1) a critical assembly for the pulsed reactor, (2) a test cell for the fast source assembly, (3) an endless tape type device for continuous production of delayed neutrons, and (4) the plutonium exponential experiment.

The modifications to the reactor cooling tower system involving both office and field engineering have been completed. It is now possible to hold up all water in the cooling tower system should it become contaminated. Also full control over the tower make-up water is now possible.

In collaboration with Plant Engineering and Planning and Reactor Operations, the secondary cooling system of the Medical Research Reactor was modified to allow 3-MW operation during the summer.

Design and engineering work on irradiation facilities continued. The first Brookhaven portable cesium development irradiator (BPCDI) was completed, and is being loaded with 100,000 Ci of Cs^{137} . Two more units are scheduled for next year. A tank irradiator with 25,000 Ci of Co^{60} was completed for shipment to Pakistan. Crashproof shipping containers for radioactive sources, are now a requirement of the Department of Transportation, and such containers for a BPCDI and a shipboard irradiator were completed. Current work includes a crashproof container and a trailer for another portable cesium irradiator that will go on tour in the United States. Servicing of irradiators at MIT and the Universities of California, Washington, and Florida was carried out. The Florida servicing included a change-over from 25,000 Ci of Co^{60} to 100,000 Ci of Cs^{137} , the first underwater use of this isotope. Fabrication will be completed shortly on two new irradiators for the Medical Department, one capable of handling blood from four animals simultaneously and one for rodents.

A marine irradiator utilizing 300 Ci of Co^{60} was completed for shipment to the Bahamas. Additional engineering support for irradiation facilities consisted of redesign of the source elevator and storage platform at HIRDL, preparation of a conceptual design for the Mid-America Radiation Research Center, design and installation of a two-pass conveyor in the HIRDL irradiation cell, and designs of controllers for "in-cell" apparatus.

Construction of the modified potassium heat transfer facility was completed and the unit was successfully operated.

The old 1000°F NaK heat transfer facility is being upgraded to constitute a 1600°F Sodium Heat Transfer Facility and will be ready next year. Design of a new test section for the mercury heat transfer loop is continuing.

Other engineering contributions consisted of flow-sheet development of power production systems utilizing MHD generators, design and construction of a laboratory-sized gas purification and circulation system, design of a capsule for the irradiation of PuO_2 fuel samples in the HFBR, and an extensive investigation into the possible use of a high-strength polymer impregnated concrete in prestressed concrete structures such as nuclear reactor vessels.

In connection with work on the pulsed reactor, codes are being developed for analysis of the fuel elements. As a spin off from this, a family of computer codes is being developed which will give the Laboratory a really advanced capability for the solution of many complex stress problems. The

power of these codes has already been applied to the concrete pressure vessel analysis mentioned above.

Work by the Chemistry Division on metallic hydrides that form or decompose at reasonable temperatures has spurred engineering interest in utilization of these materials for storage of hydrogen or for possible applications to novel power cycles.

One engineer has been with the Chemonuclear Loop, and cold test runs have been completed.

Contributions to the atmospheric sulfur pollution program include the development of grab-type air sampling from aircraft and a method of injecting sulfur hexafluoride tracer into power plant flue gases.

Pulsed Research Reactor Study

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Studies on the pulsed research reactor project have been concentrated on reference designs of two alternative concepts and supporting fuel development and physics experimental work. The two concepts under study as high-intensity neutron beam sources are a pulsed reactor in which the reactivity is periodically pulsed into the superprompt 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.

REFERENCE DESIGN OF PULSED REACTOR

Survey physics calculations were made of the neutron lifetime and critical volume for pulsed reactor cores fueled with a variety of candidate materials. The calculations of critical volume were done in a cylindrical geometry with the S_4 method, and calculations of critical volume and lifetime were done in a spherical geometry with AIM-6; good agreement between the critical volumes was obtained by the two methods. In both cases the Hansen and Roach group constants were used. The analysis was performed on cores with and without an absorbing liner between the core and the reflector. The effect of a 2-cm-thick absorb-

Table 10

Physics Characteristics of Pulsed Reactor Cores^a

Fuel	Critical volume, liters	Neutron lifetime, nsec
40 vol % PuO_2 -Mo cermet	94	61
60 vol % PuO_2 -Mo cermet	38	41
60 vol % U^{235} -Mo cermet	135	70
U^{235}O_2 ceramic	41	—
30 vol % U^{235} -Th dispersion	175	65
50 vol % U^{235} -Th dispersion	50	38

^aCoolant volume fraction, 26% (sodium); clad and structure volume fraction, 30%; core lined with 2 cm of B^{10}_4C between core and reflector; core reflected with 28 cm of stainless steel (75%) and Na (25%).

Figure 25. Core and pulse block arrangement, horizontal shaft.

ing liner of B^{10}_4C is, roughly, an increase in critical volume of 50% and a factor of two decrease in the neutron lifetime. The results of the survey calculations for selected cores with the liner are summarized in Table 10.

On the basis of the survey calculations and results from the fuel test program the 60 vol % PuO_2 -Mo cermet was selected as the fuel for this reference design.

A preliminary reactor shield zone layout has been completed for the pulsed reactor. In this design the sodium-cooled core is contained in a core vessel with the beam source moderator blocks and radial reflector outside the core vessel in a nitrogen-cooled zone. The core vessel extends to an overhead "pot" which contains the primary circulating pumps and heat exchangers. This concept facilitates access to and replacement of the primary system components. Provision is also made for periodic replacement of the core vessel, since it will be subjected to irradiation damage due to its proximity to the core.

The reflector pulse block that provides reactivity variation is carried on a wheel that rotates at ≈ 3600 rpm. A design using two rotating wheels is preferred. The primary wheel rotates at a high speed and determines the pulse characteristic while the speed of the second wheel can be varied to control the repetition rate such that a pulse is

Figure 26. Core and pulse block arrangement, vertical shaft.

produced only when the pulse blocks of both wheels pass the core simultaneously. Two alternative primary wheel arrangements have been considered. The first concept, illustrated in Figure 25, has the primary wheel rotating in a vertical plane on a horizontal shaft. This arrangement leads to a core with a length-to-diameter ratio of ≈ 0.5 , so that the pulse block can pass the core in its short distance. This concept also facilitates a two-wheel design with the second wheel arranged such that its pulse block passes behind the primary wheel. The alternative wheel arrangement is illustrated in Figure 26, and involves a rotation of the wheel in a horizontal plane on a vertical shaft. This scheme leads to a core with a length-to-diameter ratio of ≈ 1 , but makes it difficult to incorporate the second wheel in the design.

Table 11

Physics Characteristics of Accelerator-Injected^a Pulsed Reactor Cores

Fuel	Without absorbing liner		With absorbing liner	
	Volume, liters	Lifetime, nsec	Volume, liters	Lifetime, nsec
PuC	6.5	72	8.7	22
U-10 Mo	12.7	50	18.2	26

^aCoolant volume fraction, 26% (sodium); clad and structure volume fraction, 30%; lined cores have 2 cm of B^{10}_4C between core and reflector.

REFERENCE DESIGN OF ACCELERATOR-INJECTED PULSED REACTOR

Survey physics calculations were made of the neutron lifetime and critical volume for accelerator-injected pulsed reactor cores fueled with PuC and U-10 Mo. The characteristics of these cores are outlined in Table 11.

FUEL DEVELOPMENT PROGRAM

Development work was performed on a variety of candidate fuel materials including UO_2 -Mo cermet, U-10 Mo alloy, U-Nb-Zr ternary alloys, and U-Th dispersion. The 60 vol % UO_2 -Mo was tested most extensively because of the special interest in a cermet of this type containing Pu for the pulsed reactor reference design. For the purpose of the unirradiated tests, it was assumed that the substitution of UO_2 for PuO_2 in the cermet would not affect the mechanical properties.

Fatigue tests were performed on the 60 vol % UO_2 -Mo cermet at two frequencies, 186 and 14,000 cps. The low frequency tests were conducted by Battelle using the MTS machine owned by BNL. The inert gas system installed by Battelle for elevated temperature tests did not provide adequate cover gas purity, and severe oxidation of the specimens occurred during the tests. As a result further tests at the low frequency were performed at room temperature. The high frequency tests were conducted ultrasonically at Hydronautics Inc. This testing was performed in a high-purity inert gas environment at 750° F. All fatigue testing of the cer-

met was done at a mean stress of 4500 psi. Strain gauges were attached to all specimens to monitor test conditions. Prior to the start of each fatigue test the modulus of the material was measured, and this measured value was used to calculate the cyclic stress from the cyclic strain that was monitored on the specimen during the test. The test results are plotted in Figure 27, where the predicted fatigue curves are also plotted for two assumed values of the ultimate tensile strength that bracketed the range of tensile strengths previously measured for this material. The Goodman criteria were used for the predicted curves and it is apparent that all of the data are consistent with the predicted behavior. This agreement provides a basis for the cermet fuel fatigue properties used in the reference design of the pulsed reactor.

The ternary-fuel alloy development program at Battelle initially included two ternary alloys, U-31 Nb-12 Zr and U-62 Nb-7 Zr. Both of these alloys were not readily fabricable (cracking occurred during hot rolling at 1000° and 1315°C) so that tensile and fatigue specimens could be produced only from homogenized castings. Machining of the U-31 Nb-12 Zr castings resulted in two brittle fractures. Metallographic examination of the U-62 Nb-7 Zr revealed a small amount of a second phase distributed uniformly throughout the grains (contrary to expectations), and one of the tensile specimens exhibited large grain size at the region of failure. A third ternary alloy, U-20 Nb-27 Zr, was selected for its potential fabricability. Samples were cast, homogenized, and rolled without cracking at 1315°C. However, oxidation occurred during the hot rolling to the extent that the central 1/8 in. of the 3/8-in.-diam specimens showed contamination. New 3/8-in.-diam rods were prepared and assembled in 1.5-in.-o.d. $\times$ 3/8-in.-i.d. tubes of Mo to prevent oxidation of the ternary alloy. Two hot rolling passes at 1315°C achieved about a 14% reduction in the U-20 Nb-27 Zr. The measured tensile properties of these alloys are presented in Table 12.

Battelle has investigated techniques for producing dispersions of U in Th. The first attempts to produce a Th-30 vol % U dispersion were made at 1000°C, as appeared to be necessary from the literature on powdered Th. Subsequent attempts at temperatures as low as 800°C resulted in essentially fully dense specimens. The effects of sintering pressure and temperature were investigated for a Th-40 vol % U dispersion. The pres-

Figure 27. Fatigue lift of 60 vol % UO_2 -Mo cermet.

sure ranged from 5000 to 17,000 psi and the temperature ranged from 750° to 1000°C. For temperatures above 750°C the microspheres showed excessive deformation. At 750°C even the highest pressures produced negligible deformation. The density of the specimen was influenced more by pressure than by temperature so that densities >90% of theoretical could be achieved even at 750°C by using pressures of 15,000 to 17,000 psi. An attempt was made to fabricate tensile specimens by bending and cold pressing the 40% dispersion into ½-in.-diam × ½-in.-long pellets. Eight pellets were loaded into each of five tantalum tubes, which were then evacuated and sealed by electron beam welding. The five specimens were hot isostatically pressed at 1370°F and 17,500 psi for 3 hr. All of these specimens broke during machining along one of the bond lines between specimens.

CRITICAL EXPERIMENTS

A series of critical experiments, CEPFR-1A through 1D, have been performed to provide information for the reference design as well as to provide experimental verification of the analytical techniques that are being used in the reference design. Several techniques involving the use of poison liners and core cavities to reduce the neutron lifetime and to increase the magnitude or gradient of the reactivity curve associated with movement of the reflector pulse block are being studied analytically.

The calculated values for Δk corresponding to movement of the reflector block from a position centered on the bare core face to a position displaced by 1.27 cm from the center are summarized in Figure 28 for various arrangements of poison liners. From this analysis it is concluded that an absorbing liner on a portion of the bare core face increases the reactivity change associated with

Figure 28. The values of Δk corresponding to a 1.27-cm movement of the reflector block from a centered position for various core designs.

Figure 29. Plan view of the first assembly to be taken critical, CEPFR-1A.

Table 12

Tensile Properties of U-Nb-Zr Ternary Alloys at 800°F

Alloy	Modulus, 10 ⁶ psi	Ultimate strength, psi	0.2% Offset yield strength, psi	Area reduction, %
U-27 Zr-20 Nb	12.5	91,200	75,700	32.5
U-31 Nb-12 Zr ^a	12.0	36,000	—	0
U-62 Nb-7 Zr ^a	17.0	36,000	—	0

^aAs cast.

movement of the reflector block. The effect on the Δk of the absorbing liner between the core and stationary reflector is small, although, of course, poison material in this location is quite effective in reducing the neutron lifetime. Cores with cavities, as shown in Figure 28*d*, were also studied analytically; however, the convergence of the calculated reactivities were not satisfactory and no conclusions could be reached concerning the effectiveness of core cavities in enhancing the reactivity change.

The first assembly to be taken critical (CEPFR-1A) was completely reflected, including top and bottom, by a minimum of 12 in. of stainless steel. A plan view is shown in Figure 29. The nominal composition of this core was:

Material	Volume fraction
Enriched uranium	0.26
Aluminum	0.14
Stainless steel	0.42
Void	0.18

With 101 kg of 93% enriched U loaded in the core, the measured excess reactivity was \$0.92. The uniform temperature coefficient was measured and was found to be $-0.3\text{¢}/^\circ\text{C}$.

A study was made of the decrease in reactivity produced by removing steel bars $1.5 \times 1.5 \times 39$ in. high (the height of the assembly) from the reflector. The maximum effect was a decrease of 54¢ when the bar removed was near the center of the core-reflector interface, i.e., at position 28 of Figure 29.

A uranium-Lexan package that correlated fissions with damage tracks in the plastic was used to determine the fission rate about the core center. The assembly power calibration was made with the above information, and the spatial flux distribution was determined by U^{235} foils.

The neutron lifetime was measured by the Rossi-alpha technique with the use of a fission chamber located near the core-reflector interface. The observed value of the neutron lifetime was 200 nsec. The lifetime was also calculated using both the S_4 method and AIM-6. The calculated value was ≈ 110 nsec.

A section of reflector material was removed from CEPFR-1A to achieve an unreflected, open, vertical face of the core. This face was 14.8 in. high $\times$ 9 in. wide. Thus a vertical rectangular plane was formed, the outer region of which was stainless steel, and the rectangular central region

of which was the open face; core material was added to bring the partly reflected assembly, designated CEPFR-1B, critical.

The nominal composition of the core of CEPFR-1B was the same as that of CEPFR-1A; with 125 kg of 93% enriched U loaded in the core, the measured excess reactivity was \$0.55.

A trolley was built upon which the reflector block covering the open core face could be placed. Controls were carried through to the console so that the trolley bed and consequently the reflector block could be driven away from the open core face in a horizontal direction parallel to the open plane. By use of this device, the reactivity worth of the block as a function of the block position was obtained. A typical curve is shown in Figure 30, and the total block reactivity worths (the total spread of the curves) for several different reflector blocks are given in Table 13.

The neutron lifetime of CEPFR-1B with several different reflector blocks was measured by the techniques used on CEPFR-1A, and the measured values are listed in Table 13.

The reactivity worth of the 4-in.-thick stainless steel reflector block was calculated using the S_4 method in x - y geometry, and excellent agreement was obtained with the measured values.

When experiments on the CEPFR-1B series were completed, the assembly was converted to the set of cores called CEPFR-1C. These cores included an absorbing layer of ≈ 1 -in.-thick B_4C placed along the plane extending east-west from the open core face. In some cases, a 0.25-in. layer of tantalum was added to the B_4C . The movable reflector block traversed horizontally in a plane parallel to that of the absorbing layer and open core face, in most cases with a minimum distance between planes. The effect of the absorber on the curve of block worth vs position as the block was moved from directly in front of the open core face was studied as a function of block materials and sizes and open core face width.

In general, the absorbing layer decreased the total worth of a reflector block (compared to the case of no absorber) but the curves showed a slight improvement in the parabolic region, indicating narrower, more desirable, pulse characteristics.

Investigation of several neutron detectors for possible use in neutron lifetime measurements indicated that even slight amounts of hydrogenous material perturbed the local spectrum and affected the data obtained for Rossi-alpha measure-

Figure 30. Worth of the 4-in.-thick stainless steel reflector block in CEPFR-1B.

ments. It was found that the use of "spiral wound" fission chambers was questionable for measurements inside the assembly, because all such chambers on hand contained polyethylene insulation between the spirals in sufficient quantity to perturb the measurement. If the detector were outside the assembly and sampled a leakage spectrum, the perturbation as well as the detector efficiency decreased. The best data were obtained with use of a regular fission chamber design (two cylinders with close spacing). The only disadvantage with this chamber was its large volume, which required a large assembly void for insertion.

The CEPFR-1D assemblies were similar to CEPFR-1C. The purpose of this series was to determine the effect of cavities on the parabolic coefficient of the reactivity curve, α_p , for the various block materials and geometries. A series of measurements similar to those carried out on CEPFR-1C were carried out on CEPFR-1D, and a preliminary analysis of these measurements indicated the following.

(1) It appears that poison barriers are effective in increasing the value of α_p for steel and similar metal reflector blocks, but the increases observed in α_p with the amounts of poison used were not as large as desired.

(2) The use of $B_4C + Ta$ poison substantially increased ($\approx 25\%$) the α_p for a beryllium reflector block.

(3) Of all the reflector materials tested to date, the beryllium block was superior in terms of α_p

Table 13

Reactivity Worth and Lifetime in CEPFR-1B for Various Reflector Blocks

Block material	Size ^a	Worth in dollars	Lifetime, nsec
Stainless steel	A	5.75	142
Stainless steel	B	4.25	135
Polymethyl methacrylate	A	7.10	180
Beryllium	A	10.50	190
Carbon steel	A	4.75	135
No block	—	—	136
Nickel	A	6.50	134
Nickel	B	5.02	132
Stainless steel	C	1.71	130

^a A = 14.8 in. high $\times$ 9 in. wide $\times$ 4 in. thick.

B = 14.8 in. high $\times$ 9 in. wide $\times$ 2 in. thick.

C = 14.8 in. high $\times$ 3 in. wide $\times$ 4 in. thick.

and in terms of total reactivity, but at the cost of an increase in lifetime.

(4) The cavities cause local variations in α_p over short distances (1 in. and less) of block travel.

(5) Tungsten or lead are good window materials, but the introduction of a window of any kind reduces the above mentioned cavity effect.

(6) There appears to be little advantage in either the α_p values or total reactivity effect obtained by reducing the reflector block width or the open face width.

BEAM SOURCE EXPERIMENTS

The effort in the beam source experiments has been concentrated on improving the experimental techniques and synthesizing the data to provide conclusions on the optimum arrangement and geometry of the beam source moderator region.

In cold moderator experiments the neutron detector is located outside the cryostat; hence, the detector is several inches away from the surface of the moderator block under investigation. It has been shown that separation of the detector from the moderating media introduces a systematic error in the measured decay constants. A technique is under investigation that involves placing a cadmium sheet over the surface of the thermalization block inside the cryostat so that the resulting capture γ rays may be monitored instead of the emerging neutron beam. This approach should minimize the systematic effect.

Figure 31. Pulse shape and figure of merit in Lucite moderator block (20°C).

Figure 32. Pulse shape and figure of merit in polyethylene moderator block (20°C).

The measured decay constants and yields of low energy neutrons from the various room temperature source blocks that have been studied were synthesized to determine the relative performance of these sources in a pulsed reactor. The synthesis was carried out assuming that the pulsed reactor has a 50- μ sec pulse width and that a figure of merit for most experiments could be written as

$$\varphi_{\max}/W^2,$$

where $\varphi_{\max}$ is the peak pulse thermal flux intensity and W is the full width of the thermal neutron pulse at half maximum.

The decay times and relative steady-state intensities for each source block were combined to determine $\varphi_{\max}$ for various thicknesses of polymethyl methacrylate and polyethylene using Kley's formulation

$$\varphi_{\max} = \varphi_{s^{\infty}} [1 + \exp(-50/\tau)] \mu\text{sec},$$

where $\varphi_{s^{\infty}}$ = the relative steady-state flux from the thermalization blocks, and

τ = the block decay constant.

The thermal pulse width at half-maximum (W) emerging from the thermalization block for a 50- μ sec reactor pulse was calculated assuming

$$W = 50 + \tau \ln[1 + \exp(-50/\tau)] \mu\text{sec}.$$

The figure of merit as a function of thickness of polymethyl methacrylate (Lucite) and polyethylene blocks were determined and are shown in Figures 31 and 32. It can be seen from these figures that the figure of merit peaks at 1.2-in. thickness of polymethyl methacrylate and 0.8-in. thickness of polyethylene, and that at the peak the polyethylene figure of merit is about 50% greater than that for the polymethyl methacrylate. Since the polyethylene has about 50% greater hydrogen density than that of polymethyl methacrylate this points up the importance of using as high a hydrogen density moderator block as possible. It is also noted that for a 50- μ sec reactor pulse, thermalization blocks 1 in. thick or less introduce only a very small broadening of the emergent pulse.

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