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BROOKHAVEN NATIONAL LABORATORY

Annual Report *Nuclear Engineering Department*

December 31, 1965

RELEASED FOR ANNOUNCEMENT
IN NUCLEAR SCIENCE ABSTRACTS

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WARREN E. WINSCHÉ, Chairman

F.T. MILES, Deputy Chairman

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BROOKHAVEN NATIONAL LABORATORY

Associated Universities, Inc.

Upton, New York

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SUMMARY

Settled Bed Reactor

(04-50-90-01-1)

During the past year the physics of the ordered bed, cermet fueled fast breeder has been studied. The work was done in cooperation with others towards the objective of an economic analysis of a 1000-MW(e) breeder which features counter-current fuel management. In this scheme, blanket fuel is moved inward toward the core center as its fissile content increases. Fresh blanket material is added at the outside of the reactor while spent fuel material is discharged at the reactor center. With good breeding gains and high fuel burnup, only fertile material needs to be added to the blanket when steady-state conditions are approached. Otherwise, spiking of this material with fissionable material is necessary. Studies of 1000-MW(e) settled bed reactors show that spiking becomes unnecessary for U^{238} metal if 7% burnup can be attained. For carbide and cermet (80% UO_2 by volume in stainless steel) fuels the required burnups are 11 and 19% respectively.

The dynamics of the randomly packed settled bed under temperature perturbations have been studied. Because of the strong negative sodium coefficient provided by the plenums required for fluidization, the reactor is safe against strong perturbations in temperature. It is clear that, by proper mechanical designs, this safety feature could also be obtained for the conventional pin type fast reactor and studies along these lines are therefore being continued.

Cermet fuels containing 60% UO_2 in a stainless steel matrix have been procured and are being irradiated in the Engineering Test Reactor. An interim α - γ facility for examining the irradiated fuel is under construction.

Stainless steel balls (to simulate cermet fuels) have been subjected to load under hot sodium to investigate sintering. Under certain conditions some of the balls stuck together. Coatings are being studied.

Sodium has been circulated through ordered beds of stainless steel balls to study bed stability with thermal cycling.

Techniques for handling settled beds – both random and ordered – are being examined. Experimental methods of studying bed packing have been explored. One basic technique consists of embedding small opaque markers at the centers of transparent spheres. The distribution of sphere centers is measured optically.

The pressure drop of water flowing through large ordered beds is being measured with sphere size, spacing, void fraction, and bed height as variables.

Reactor Physics Division

(04-01-20-02-1, 04-40-01-01-1, 04-50-50-01-1, 05-03-01-03, 04-50-10-03-1)

During the past year, the experimental program was completed on 3% enriched $U^{233}O_2$ - ThO_2 fuel rods in water-moderated exponential experiments. Preparations for two series of heavy water-moderated exponential experiments were started. The first of these experiments will involve clustered fuel rods and an organic coolant to provide the reactor physics data urgently needed for the design of large, high conversion ratio power reactors. The completed experiments involved two poisoned water concentrations at moderator-to-fuel volume ratios of 1:1, 1.38:1, 1.71:1, 2.19:1, 3.0:1, and 4.27:1, and one poisoned water concentration at a volume ratio of 6.8:1, in addition to the clean experiments previously reported. The measurements included bucklings, reflector savings, and flux traverses. A previously noted discrepancy between theory and experiment on reflector savings vanished when radial flux traverses were carried out sufficiently far from the base of the core. A number of miniature lattices with 16-in. fuel rods were assembled to measure microscopic parameters, including thermal disadvantage factors and ratios of epithermal to thermal activation of thorium. A new technique for the measurement of fast fission is reported.

In the minimum reflection critical facility a series of critical experiments was carried out on near homogeneous graphite cores with highly en-

riched U^{235} as the fuel. Measurements of buckling, neutron lifetimes, thermal disadvantage factors, and temperature coefficients of reactivity were carried out for a number of assemblies with carbon-to- U^{235} atom ratios ranging from 22,900 to 5730 to 1. The agreement with old theoretical calculations based on the GAM and THERMOS codes is extremely good. In addition, an intermediate energy loading ($C/U^{235} = 950$) with a critical mass of 60 kg was completed.

Start-up of the HFBR was accomplished on October 31, 1965. The Reactor Physics Experimental Group is assisting the Reactor Operations Division in start-up experiments which will take 4 to 6 months for completion. A re-examination of *Theoretical Possibilities and Consequences of Major Accidents in Large Nuclear Power Plants* (WASH-740, 1957) was completed at the request of the AEC. It was concluded that any new report based on the same assumptions as WASH-740 would not differ substantially from the original.

Other experiments reported include those on diffusion parameters of polyethylene and water, diffusion coefficient anisotropy in slab lattices, and studies of control rod configurations. Measurements on the Beam Experiment Test Assembly were completed. This facility tests the effect of fuel element modifications on the quality of external thermal neutron beams in swimming pool reactors. Comparative studies of methods of measuring thermal and epithermal cross sections of transuranium elements indicate the utility of reactivity measurements in thermal assemblies. Detailed planning of such experiments is under way, the main problem being the procurement of the highly active samples in suitable form. Experiments were carried out which proved the feasibility of measuring packing densities of fuel spheres in a settled bed reactor by critical experiments. Neutron Source Reactor II was taken to its design power of 100 kW on August 10, 1965, and Neutron Source Reactor I is being modified for operation at the same power level.

The analysis of the BNL thorium- U^{233} lattices was continued. A considerable effort was devoted to D_2O -moderated lattices to aid in the design of future experiments. Specifications for plutonium-fueled, D_2O -moderated lattices were completed. A review of all pertinent cross-section data is being carried out in collaboration with members of the Reactor Cross Section Evaluation Group. A pre-

liminary analysis of the minimum reflection U^{235} -graphite slab lattices was completed. The results for k_{eff} and critical buckling show excellent agreement with the experiments.

Extensive work was carried out on the development of codes including HAMMER (in collaboration with J. Suich of the Savannah River Laboratory) and MOCA-2A (in collaboration with R. Dannels of WAPD).

Among the theoretical accomplishments were improvements of resonance absorption theory for heavy moderators, studies of the effect of fuel cladding on Dancoff factors, and a study of the anisotropy of thermal neutron transport in slab lattices. Improvements in the theory of resonance capture in clustered lattices have been explored.

The principal subjects of research in the Theoretical Reactor Physics Group in 1965 were neutron transport in thermal, fast, and intermediate systems, reactor kinetics, and the dynamics of fluids and hard spheres. The research led to 22 publications by members of the group. In neutron thermalization, research was particularly successful in elucidating the nature of the discrete spectrum of decay constants, and its connection with moderator type. Also, a solution to the thermal Milne problem with absorption was obtained.

Studies of transport in the fast and intermediate regions have led to improvements in the theory of resonance absorption in lattices and to the beginning of a program designed to test conventional recipes and cross-section sets. In reactor kinetics, new methods were applied to the study of stable, periodic solutions, and new criteria for boundedness were discovered.

Contributions in fluid dynamics consisted of an analysis of the flow of a viscous, incompressible fluid past a disc, a study of the flow of boiling water in heated pipes, and a solution for the slow motion of a viscous fluid through channels of various shapes. The difficult problem of the arrangements produced by the random packing of hard spheres in a container has begun to yield to computer "experiments" of considerable subtlety. The method of Clancy yields results quite close to those obtained in random "loose" packing of spheres.

A code NO MURK was completed to solve space-dependent nonlinear kinetics problems. It has been applied to the study of transients in fast reactors caused by a sudden change in coolant temperatures. Criteria for nonlinear stability have been explored.

The Neutron Cross Section Compilation Group completed Volume III of the second supplement to BNL 325 and it was distributed in August. Work began in August on the preparation of Volume II. The data tape (SCISRS) now contains over 200,000 data points. A number of potential users from European centers were trained in the use of SCISRS at the Sigma Center. A collaborative arrangement has been reached whereby the Sigma Center will provide the Nuclear Data Group at Oak Ridge with neutron resonance parameters.

The activities of the Reactor Cross Section Evaluation Group for the last report period included the establishment of a center for evaluated nuclear data, parametric fitting of the slow and fast neutron cross-section data, and a theoretical treatment of the fluctuations observed in fast neutron cross sections.

The Evaluated Nuclear Data File (ENDF), located at BNL, is intended to be a common link among the many laboratories that have evaluated cross sections for use in reactor calculations. The ENDF is a tape-card system that provides for the exchange of cross section libraries among laboratories. The programs necessary to store and transmit cross section data have been completed. Programs to retrieve the data in selected forms are in progress.

Parametric fitting to experimental cross sections have been performed at low energies with the use of the Breit-Wigner single level formula and at high energies with the optical model. Elements in the range from sodium through the heavy elements have been included in the study.

The direct conversion work done in the Department is quite diversified, being a representative cross section of the major types of direct conversion work being pursued in this country and abroad, including gaseous plasma MHD, liquid metals MHD, and fuel cells.

In the decision as to the suitability of a particular project, the criteria have been that it be related to nuclear energy, have results or by-products of use to nuclear technology, and involves techniques which Brookhaven has developed or possesses unique capabilities. All present or projected investigations satisfy some or all of these criteria. For example, both of the nonequilibrium plasma MHD programs make use of fission fragment induced ionization or energy deposition in the work-

ing gas. This takes place in a critical assembly (either part of a main reactor heat source, or an auxiliary reactor) and involves a fission product source developed originally in the Radiation Division of the Department for chemonuclear work. The project involving a thermal equilibrium plasma has a working fluid of fissionable material. In the liquid metal work (e.g., the liquid metal slug generator), the concepts are dependent on advanced boiling metal reactors being developed, and are proposed as either earth-bound topping cycles or space power plants. The MHD bearing concept involved in the solid slug generator shows promise as a bearing capable of working efficiently at very high temperatures in hermetically sealed devices. The Pb-PbBr₂-Br₂ fuel cell concept requires a liquid lead cooled reactor as its primary power source.

In all of these efforts the attempt is being made to understand the underlying mechanisms involved; for example, in connection with the fission fragment induced conductivity, the basic nature of a fission fragment track is being examined, while in connection with the fuel cell work, an inquiry is being made into the various electrode polarization processes tending to reduce the efficiency from the ideal value.

A concurrent evaluation of the economic and engineering aspects of the various direct conversion schemes is carried out as these programs develop.

The list of published papers of this group for the past year reflects the diverse nature of the work, being published under the aegis of such different organizations as the Electrochemical Society, the American Physical Society, the American Nuclear Society, and the American Society of Mechanical Engineers.

In the area of advanced testing and research reactors, a comparative study has been made of different design concepts for a pulsed fast reactor capable of operating at power levels an order of magnitude above that of the SORA reactor.

In anticipation of the start-up of the HFBR, a detailed analysis of its expected transient behavior and a re-analysis of accident dynamics were completed. On October 31, 1965 the HFBR achieved criticality.

The Evaluation and Technical Assistance Group continued to assist the AEC in the areas of program review and evaluation of submitted proposals. An evaluation of the research and development program for the study of SNAP fuel element

re-entry burnup was completed. This work essentially ended BNL's work on the Nuclear Safety Program Review. Two proposals, (1) the super temperature dual (STD) flow turbine system, submitted to the Systems Analysis Branch, and (2) the remote rotor electric drive, submitted to the NYOO, were evaluated and a report was submitted to each of these offices. Chapters on capital costs and operation and maintenance costs for Vol. 1 of the new *Nuclear Cost Guide* were completed. This new volume is essentially a revision of the *Cost Evaluation Handbook* (TID 7025) published in 1962.

The Evaluation and Technical Assistance Group also participated in a number of design and evaluation studies of concepts generated within the Department. An economic study was made of the use of a lead bromide chemical direct conversion device as a topping unit for a nuclear power plant. This study pointed up the need for extensive engineering work to establish the feasibility of this promising concept. A study was initiated to determine the feasibility of producing heavy elements such as Pu^{238} and Cm^{244} utilizing neutrons in a resonance energy range (epithermal) rather than thermal neutrons. This proposition has been tested with two computer programs designed for the purpose, and in all cases the superiority of the epithermal irradiation over thermal irradiation has been established. A study was made of the feasibility of substituting Co^{59} for some of the structural materials normally used in the fabrication of power reactor control rods to produce salable Co^{60} . Early calculations have shown that significant amounts of high specific activity Co^{60} could be produced without altering the core design or changing the mode of reactor operation. A computer code is being prepared for use in the study of Po production from Bi irradiation. An examination of the rotating fluidized bed reactor concept indicated that this reactor could produce extremely high fluxes for significant time periods and may warrant further consideration as a research facility.

Chemistry and Chemical Engineering Division

(04-20-04-01-1, 04-40-03-01-1, 04-40-04-02-1,
04-60-10-01-1, 04-60-40-03-1, 05-05-03-01)

In studies of the radiation stability of fluorocarbons, striking differences in sensitivity among

different structure types were found. In one case, that of perfluorobicyclohexyl at high temperature, radiolysis proceeds by a chain reaction, with consequent very high product yield ($G \approx 20,000$). Some other alicyclics, however, are remarkably stable, even better than perfluoroaromatics. At 450° , perfluorocyclohexane has a G value of only 3 molecules destroyed per 100 eV of gamma radiation absorbed.

Irradiation of carbon tetrafluoride showed greater stability than other workers have reported. The discrepancy is apparently caused by the presence, in others' work, of oxygen. Both the amount and the nature of the products were found here to be quite sensitive to oxygen content. At 350 ppm oxygen (our lowest yet achieved) G is 1.4×10^{-2} for formation of C_2F_6 , the predominant product.

In the study of electrode kinetics in systems of possible use in the release of stored energy, it was found that the thallos-thallic Redox system does not appear to be useful as a potential mediator in oxygen reduction. Kinetic studies of electrodes in this system have, however, revealed some new and interesting phenomena in the behavior of smooth platinum electrodes in Redox systems.

Research has been begun on the properties of selected metal-hydrogen systems, with a view to the reversible storage of electrolytic hydrogen. Both kinetic and equilibrium studies are in progress. Emphasis will be placed on alloy systems with a fairly high hydride decomposition pressure and rapid attainment of equilibrium. The system Ni-Mg- H_2 has been found to show some promise.

Additional results have been obtained on the thermodynamic properties of high temperature systems by electrochemical methods. Free energies of mixing were determined in the fused-salt systems KCl-MgCl_2 , KCl-CaCl_2 , and KCl-SrCl_2 , and large negative deviations from Raoult's law were found. Uranium sesquicarbide, U_2C_3 , was found by emf measurements to be the stable carbide in equilibrium with carbon at 1000°K . The systems Ag-AgCl , Ag-AgBr , Pb-PbCl_2 , and Zn-ZnCl_2 were studied by a chronopotentiometric technique and solubilities were determined. In the latter two cases the dissolved species is the diatomic doubly charged ion M_2^{+2} .

The free energy of formation of UI_3 at 320° and 370°C has been determined via emf measurements on the solid state cell $\text{U, UI}_3 | \text{NaI} | \text{AgI} | \text{Ag}$. The respective values thus obtained were -102.2 ± 0.6

and -99.0 ± 0.6 kcal/mole compared with the literature values of -107.9 and -105.7 kcal/mole, which are many years old and were calculated from free energies of other reactions.

The apparatus for studying the reaction of graphite and H_2 has been much improved with the use of (a) dc power supply which eliminates the filament temperature fluctuations, and (b) a double-trace oscilloscope to measure the temperature photoelectrically and the current at a response time of 1 msec. With this apparatus, it was found that between 2000° and $2650^\circ K$ and between 0.01 and 1.0 atm, the reaction occurred on the surface and the rate, which varied by a factor of 10^3 , was proportional to the H_2 pressure and to the $\sqrt{K_D}$, where K_D is the dissociation constant of H_2 . Methane is the only product below $2650^\circ K$ and appears to result from the elimination of CH_3 radicals at the surface.

Nuclear graphites have been pulverized and the upper limiting specific surface area related to the total surface area of closed pores in graphite. For TSX graphite, these pores appear to have an average width of 15 Å and an average length of 15 μ .

The dissolution step of the Nitrofluor process for treating reactor fuels, to recover uranium and plutonium, was successfully demonstrated on the kilogram-scale with U-Zr and U-Al alloy fuels and with UO_2 fuel clad with stainless steel. The dissolutions were made in a controlled manner in Monel equipment using the nonaqueous solvent $NOF \cdot 3.1HF \cdot <0.1N_2O_3$ which boils at $95^\circ C$.

The next process step – the separation of the uranium from the dissolved fuel materials – was proven on a gram scale with both alloy fuels. After the dissolver solution was evaporated, $>99\%$ of the uranium was volatilized as UF_6 by treating the solid residue with BrF_3 at $150^\circ C$. Alternatively, the uranium was removed as $NOUF_6$ by contacting the solids with NOF gas at $400^\circ C$. The volatilization of UF_6 from dissolver solution containing excess HF was achieved by the addition of F_2 .

In fundamental corrosion studies employing sensitive wire probes, it was shown that nickel is superior to Monel in solutions of $N_2O_3 \cdot 12.6HF$, which is an alternate dissolving agent and is formed during production of the solvent mentioned above.

During the past year the pilot plant studies on the fluidized bed volatility reprocessing of reactor fuels have centered on the further development of

the $HF-O_2$ head-end step for removing the stainless steel or Zircaloy cladding. This step is followed by a reaction with F_2 to convert U and Pu to the volatile hexafluorides. The two-step process was successfully demonstrated using small clusters containing as many as 16 Yankee-type fuel rods. Bench-scale work was carried out in support of the pilot plant program to resolve problems of bed recycle, bed caking, and chromium volatilization.

Fluidized bed reprocessing studies were also carried out with graphite matrix fuel containing both U and Th as carbides. The graphite matrix is first reacted with O_2 and removed as CO_2 . The U is recovered, by reaction with F_2 , as UF_6 . A small percentage of the uranium was trapped within the nonvolatile ThF_4 and an intermediate pyrohydrolysis step was required to achieve satisfactory uranium recovery.

Conversion of high-level wastes to phosphate glass offers a promising means of incorporating fission products in a stable media suitable for long-term storage. In the Brookhaven process, phosphoric acid is mixed with the waste to prepare a feed solution which is then reduced in volume by evaporation and converted to glass by heating to $1200^\circ C$ in a platinum crucible. Development of the process as a continuous operation was greatly simplified because an all-liquid system is involved. The pilot plant used to study the phosphate glass process on a realistic scale, with simulated waste, continued to operate as needed throughout the year. Data obtained from the operation formed the basis for the design of a full-scale demonstration prototype now being constructed at Pacific Northwest Laboratory (operated by Battelle Northwest at Richland, Washington) and scheduled for operation with high-level radioactive wastes in 1966. A full-scale model of the prototype evaporator is now being tested at Brookhaven. The program was extended to include studies on phosphate glass formation from waste with compositions reflecting higher uranium burnup in the fuel.

A new program was established for the purpose of developing a method for treating high-level wastes from uranium and plutonium recovery by the fluidized bed volatility process.

One of the major concerns in reactor safety is the nature and extent of the radioactive nuclides likely to be released in the event of an accident. A continuing program is under way here to provide fundamental data on the chemical reactions, mecha-

nisms of release, and transport behavior of the fission products emanating from irradiated nuclear fuels. These data are needed to assess realistically the probable consequences of an accident under a wide variety of environmental conditions.

As part of this program, studies were carried out on the release of iodine from metallic U and hypostoichiometric UC into helium. Varying proportions of two uranium subiodides together with atomic iodine were released at temperatures ranging from 1200° to >2500°C. An analytical study of iodine behavior in sodium was undertaken to establish the probable nature and extent of the iodine released from this important liquid metal coolant. These calculations showed that sodium iodide is fairly nonvolatile compared to sodium, and it should concentrate in the liquid phase as sodium vaporizes. Sodium iodide is expected to be the major species, even under oxidizing conditions. In those environments likely to be encountered in water reactor accidents, some of the iodine may be converted to organic compounds such as methyl iodide. However, the fraction of the iodine existing as methyl iodide should be quite small since recent studies show that it undergoes substantial decomposition in a combined oxidizing and radiation environment.

The work of the Heat Transfer Group was again devoted almost entirely to the study of forced convective heat transfer to liquid metals, in both single-phase and two-phase flow.

One subject in which the group has maintained an interest for several years is that of heat transfer to liquid metals flowing through annuli. During this past year an analytical study of the effect of eccentricity on heat transfer in annuli was completed. An experimental study of eddy diffusivities for both heat and momentum transfer in flow of Hg through annuli was also pursued, the results of which will have fundamental significance beyond the particular geometry and liquid metal used in the experiment.

A second area of interest is that of heat transfer for flow of liquid metals through rod bundles. The results are directly applicable to the design of fast reactor cores and liquid-metal heat exchangers. In this past year a test section, for 90° cross flow, was installed in a convective NaK loop, and local heat transfer coefficients were measured on test rods at eight different locations within the rod bundle. Tests were made both with power on the test rod

only and with power on all rods in the bundle. Next year a new test section for 45° cross flow will be installed for measurements with oblique flow.

A major project in the Heat Transfer Group is the study of forced-convection, boiling liquid-metal heat transfer. The immediate objectives are measurement of temperature profiles, heat fluxes, and pressure drops for boiling two-phase flow of K in round tubes. A new series of experiments was carried out at temperatures up to 1515°F. Results confirmed an interesting phenomenon first noted in the initial series of tests on this loop – that, for boiling two-phase annular flow of liquid metals, there can exist a nonequilibrium inverse temperature profile in the fluid stream. A theory has been proposed to explain this phenomenon which indicates that while this effect may be negligible for ordinary fluids, it is important for alkali metals.

The Heat Transfer Group has continued to be responsible for the publication of the *High-Temperature Liquid-Metal Technology Review*. This is a bi-monthly review of current research and development in the United States sponsored by the AEC, NASA, and the Air Force, in the area of high-temperature liquid-metal technology.

An investigation is being carried out on rotating, gas-fluidized beds under high g 's, as cylindrical annuli, with particular respect to their application as fuel beds for high-power-density nuclear reactors. Such a fuel system, with the coolant flowing radially inward, would provide a very large surface for transfer of heat to the high-velocity coolant, and problems of structural integrity of the fuel would be minimal. The application of primary interest is in rocket propulsion systems. During the past year, the work has centered on the determination of the performance characteristics of fluidized beds with very high gas flow rates and subjected to high g forces. This has included (1) determination of the minimum fluidization velocity and extent of fluidization and bubbling, and (2) determination of particle-to-gas heat transfer coefficients in packed and fluidized beds.

Radiation Division

**(04-40-04-04-1, 05-05-03-01,
08-04-01, 08-05-01)**

The Radiation Division's activities are diverse, ranging from fundamental research studies on the

interaction of radiation with matter to the design of large-scale irradiators for industrial applications. There is frequent overlap between the different groups within the Division but for the purposes of this report the Division's scope can be subdivided into four sections: Radiation Research, Radiation Processing, Radiation Engineering, and Exploratory Research.

The Radiation Research effort is concerned with mechanism studies in radiation-initiated reactions of organic substances. Much of the effort is in the area of polymerization where the objective is a greater understanding of the reaction intermediates, their nature (i.e., free radical or ion), and the importance of physical structures in the behavior of these intermediates. There is a strong emphasis on the kinetics of liquid-phase and solid-state polymerization, electron spin resonance spectroscopy, and dielectric loss determination.

The Radiation Processing effort is directed toward the use of nuclear energy for industrial chemical processing. This objective is pursued in such basic chemical problems as the radiolysis studies on liquid ammonia and the fixation of nitrogen. It extends to the engineering-scale exploration of the potential of a radiation process for ethylene polymerization and copolymerization. A chemonuclear study is directed toward determining (by experimental programs and analytical evaluations) the possible application of nuclear reactor energy for chemical processing.

The Radiation Engineering effort is concerned with the problem of engineering processes and process equipment in which radiation is an integral part. It is concerned with source and facility design, handling and shipping problems, the measurement of radiation, and preparation of a Radiation Engineering Handbook.

The Exploratory Research group is composed of scientists doing both individual research and research complementary to the rest of the program. At present there are studies in progress of a gamma monochromator, the effect of radiation on fixed and settled beds, the design of photoreaction vessels, and an alpha source calibrator.

Work has continued on determining the mechanism of radiation-induced polymerization in the solid state. Data have been obtained on the effect of pressure on the rate and extent of trioxane polymerization. It has been found that the reaction initiates at the surface of crystals, propagates across

crystal interfaces, and continues to grow in a direction dictated by the polymer's crystal habit rather than along the *c*-axis of the second crystal.

ESR measurements on solid amides have clarified an understanding of the effects of oxygen diffusion on polymerization rates.

A detailed analysis of the effects of minute amounts of water on radiation-induced styrene polymerization suggests that as water is removed, the mechanism changes from free radical propagation to cationic and then to simultaneous cationic and anionic propagation.

In studying the radiolysis of substituted toluenes, a very strong isomer effect was noted when an electropositive substituent is meta to the methyl group.

In the chemonuclear program considerable capsule data have been obtained in fission fragment fixation of nitrogen in the N_2-O_2 system. Preliminary experiments on the synthesis of ozone have shown that the steady-state concentration of ozone has marked dependence on dose rate.

The technology for producing ultrathin chemonuclear fuel has advanced considerably. A "standard" research type fission fragment source is being fabricated and supplied to other laboratories working in this field. An extensive thermal analysis of a honeycomb chemonuclear fuel element has been carried out.

Work on the construction of the Chemonuclear In-Pile Research Loop has proceeded steadily.

Considerable data have been obtained on the gamma-ray-induced polymerization of ethylene and ethylene copolymers and on the characteristics of the radiation-produced products.

All facilities of the High Intensity Radiation Development Laboratory have operated satisfactorily this period. The irradiation cell has operated with a 600,000-Ci Co^{60} plaque source, one of the most intense in the world. Experiments have been conducted to determine the limitations and optimum characteristics of the source-conveyor system.

The first volume of a Radiation Engineering Handbook has been published as a BNL report entitled "Computational Methods of Gamma Irradiation Design."

Studies have continued on a variety of dosimetry techniques including a very thin polymethyl methacrylate dosimeter, a miniaturized Fricke dosimeter, and a flow chemical dosimetry system.

A new gamma calorimeter has been constructed and several BNL standard sources have been cali-

brated. It is estimated that the curie content of Co sources can be determined by this method with an accuracy of $\pm 2\%$.

Several theoretical problems were under study during the year. One predicts the effects of turbulence on the kinetics of a particular radiation-induced reaction and another examines the validity of the quasi-stationary state approximation for intermediates in complex reaction sequences in the presence of spatially nonuniform initiation.

Hot Laboratory Division (05-05-03-01, 05-02-05-01, 08-03-01)

In the area of analytical chemistry research, from a study of mixed chloride-bromide complexes with palladium, have come the stepwise formation constants, the relative amounts, the spectrophotometric absorption maxima, and molar absorptivities of the various species. Study of the synergistic effect of various β -diketones on the extraction of UO_2^{+2} , Cu, Sc, and In has revealed some surprising effects. Stability constants in molten dimethyl sulfone were measured for the nitrate complexes of lead and cadmium and for palladium chloride complexes, as were the physical properties of the solvent. An equation was found which relates the current, time, and kinetic parameters to the intensity of light emitted during chemiluminescence produced by the electrogeneration of anion and cation radicals of aromatic hydrocarbons at a single electrode. Mechanisms and rate constants were determined for the disproportionation of U(V) in acetate buffer without and with added EDTA, which changes the disproportionation from second order to first order.

In the area of isotopes research a study of the chemistry of tellurium is shedding light on previous discrepancies concerning the ratio of oxidation states of radioiodine formed by the decay of Te^{132} under various conditions; yields of I^{132} generators are becoming predictable and understood; data on which to base a tellurium isomer generator are being accumulated. New compounds and complexes of technetium are being discovered. The relative lack of effect of spin change on the cross section of reactions with low-energy tritons is surprising. The excitation functions of the $\text{Ar}^{40}(\alpha, 2p)\text{Ar}^{42}$ and $\text{Ca}^{48}(\alpha, p2n)\text{Sc}^{49}$ reactions and the yields of the $\text{Ca}^{48}(\alpha, \alpha n)\text{Ca}^{47}$ and the $\text{Sb}^{121}(\text{He}^3, n)\text{I}^{123}$ reactions

were measured. Zirconium phthalocyanine Szilard-Chalmers targets were prepared. The decay scheme of Ir^{196} was further investigated. Limits were put on the half-life of Sc^{48m} and on the extent of ternary fission.

Production of special isotopes continues to increase markedly, largely as a result of the continually increasing demand for Tc^{99m} , an isotope with nuclear properties that are particularly useful from a medical standpoint. Shipments made in 1965 were double those made in 1964.

Metallurgy and Materials Science Division (04-40-02-01-1, 05-06-01-02)

Both applied and fundamental research were performed in this Division during 1965. Applied research included studies of corrosion by boiling Hg and Na and by liquid Na-Li alloys, studies of effects of irradiation on body-centered cubic metals, determination of the high-temperature properties of reactor core materials, development of superconducting devices, and monitoring of the materials behavior in both the BGRR and the HFBR. Fundamental research programs included experimental and theoretical studies of the properties of liquid metals and superconductors. The highlights in each of these areas are given below.

Corrosion by boiling Hg is being studied because of the considerable current interest in Hg as a heat transfer and working fluid in Rankine-cycle turbines to be used in compact nuclear power devices in space vehicles. During 1965 it was determined that unalloyed Ta is completely corrosion resistant to boiling Hg at 640°C ; Hg was boiled in a thermal convection loop of this material for $\approx 20,000$ hr without detectably corroding it. Cb-1 Zr, however, was penetrated by Hg even in a loop that had been annealed after fabrication; apparently thermal stresses were sufficient to cause this stress-sensitive penetration. Stress-sensitive attack of samples of a Ta-8 W-2 Hf alloy by Hg and of unalloyed Cb by Pb-Bi eutectic was also discovered.

Corrosion by boiling Na is being studied because of the advantages the high boiling point of this fluid offers in space power systems. All refractory-metal alloys are corrosion resistant to low-oxygen (hot-trapped with Zr) Na as long as they contain Ti, Zr, or Hf as oxygen stabilizers. When, however, a

stabilized refractory-metal alloy (Cb-1 Zr) contains sufficient oxygen to react with all or most of the Zr, it is no longer corrosion resistant to Na boiling at 1200° to 1315°C. Cermet tabs containing Ni binders were corroded by Na at 1205°C because of selective dissolution of the Ni by the Na.

Corrosion by liquid Na-Li alloys is being studied because the increasing solubility of liquid Li (with its higher cross section) in liquid Na with increasing temperature offers the possibility of internal, automatic control in a fast reactor system. Preliminary studies indicate no corrosion or mass-transfer of stainless steels by Na, Na-15 wt % Li, or Li after 4700 hr of operation at 600° to 700°C, as determined by radiography.

Both mechanical properties and microstructures of irradiated Fe are being studied, since detailed knowledge of the behavior of this material under irradiation is essential to its proper use in reactors. There is a pronounced difference in the ductile to brittle transformation between Fe irradiated at 70°C, which becomes brittle at -146°C, and Fe irradiated at -70°C, which does not become brittle at any temperature so far tested. This is probably due to a difference in interactions between dislocations and point defects at the two temperatures. Carbon is removed from solution in α -Fe by fast irradiation. A program is under way to study the effect of periodic annealing on the impact transition of irradiated steels with the hope of devising a means of preventing their room-temperature embrittlement under irradiation. Irradiated Fe contains defects invisible to the electron microscope which are capable of affecting the yield stress; these can be converted by adding oxygen to visible defects, which develop into dislocation loops upon heat-treating the Fe. Nitrogen, carbon, or hydrogen, however, cannot effect this conversion. Increasing the concentration of the visible defects by changing the composition of the Fe or by increasing the irradiation dose lengthens the annealing time required to restore the hardness to its pre-irradiation value. This observation is the basis for initiating the above-mentioned annealing program. Irradiation-induced defects in W have been directly observed with use of a field ion microscope.

The high-temperature properties of reactor core materials are being studied to provide information applicable to their use in reactors. The kinetics and thermodynamics of the exchange of Br, Rb, and Cs with their lamellar compounds are being deter-

mined. Surface processes (graphite particle size) and temperature affect the rates of exchange. Thermodynamic data were obtained on the Th-B system by using electrochemical cells. Electrical measurements on ThC have shown that its electrical resistivity increases with the C content, from ThC_{0.74} to ThC_{0.94}. The Hall coefficients increase (negatively) similarly; they indicate ≈ 0.2 free electrons per Th atom.

Materials monitoring programs are under way at the BGRR and the HFBR to determine the effects of the periodic annealing program on the graphite in the BGRR and the corrosion and mechanical properties of the Al alloys in the HFBR. Many samples of BGRR graphite are now approaching their preirradiation dimensions; the height of the reactor has decreased and the width of the central air gap has increased as a result of the periodic annealing treatments. No stored energy releases have been found in the reactor graphite at 200° or 350°C; the total (high-temperature) stored energy does not exceed the specific heat of the graphite.

The physical properties of the alkali metals and liquid alloys of Na are being determined to further understanding of the atomic and electron interactions in liquid metals and alloys. Data have been obtained on the thermodynamic properties, densities, electrical resistivities, and thermoelectric powers of selected systems. Both the electrical resistivities and the densities of liquid Pb-Sn alloys have been found to be a smooth function of composition. The thermoelectric power of Na does not change upon melting. The thermoelectric powers of K, Rb, and Cs all increase upon melting; the extent of this increase becomes greater as the atomic number increases. Theoretical calculations of the structure of liquid Na have been made with use of a long-range oscillatory potential; the calculated structure is in good agreement with experiment. Electromigration and diffusivities of Ag, Cd, and In in liquid Bi have been determined.

An interdepartmental superconductivity program has been established between the Nuclear Engineering, Physics, and Accelerator Departments to provide interplay between the research programs and the development of superconducting devices. Theoretical calculations have yielded correct, detailed differences between strong and weak coupling superconductors. They have also predicted that the critical temperatures of thin super-

conducting films rise sharply with decreasing film thickness below 30 Å. This rise has been observed experimentally in both Al and W films. Transition temperatures were also found to be a function of x-ray line broadening; they increased with the oxygen content of the film. A theory relating ac susceptibility, surface critical currents, and bulk magnetization curves has been developed. Studies of irreversible superconductivity have shown that the properties of remnant flux in Nb, Pb, Bi, Sb in Sn, and Pb in In can be explained by postulating the existence of a surface barrier in the form of a surface shielding current.

A high-field solenoid with a conical base has been built and is being tested; is is expected to produce fields up to 130 kG. Field gradients considerably higher than those now in use can be obtained by using superconductors. The performance of solenoids of Nb₃Sn can be greatly improved by

operating them at temperatures at which He is a superfluid (below 2.2°K).

Engineering Division

**(04-4-01-01-1, 04-40-02-09-1, 04-50-50-01-1,
08-04-01, 04-40-04-04-1, 04-40-04-02-1,
04-01-20-02-1, 04-40-03-01-1)**

The Engineering Division contributed $\approx$ 100,000 man-hours to the support of various departmental programs during 1965. The majority of this support was in the design, construction, and operation of experimental facilities used for research in radiation processing and engineering, liquid-metal heat transfer, experimental physics, materials for containing liquid metals, and advanced reactor concepts. The Division also contributed to various national technical committees and the *High-Temperature Liquid-Metal Technology Review*.

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*AEC budget activity numbers.

NUCLEAR ENGINEERING DEPARTMENT

BROOKHAVEN NATIONAL LABORATORY

ORGANIZATION CHART

DECEMBER 1965

Settled Bed Reactor

Neutron Physics

COUNTERCURRENT FUEL MANAGEMENT

In the countercurrent fuel management method fissile material produced in the blanket of a breeder reactor can be used directly in the core without intermediate reprocessing and refabrication steps. When the breeding ratio is sufficiently high, the total fissile material required by the core can be furnished in this way, provided that the fuel can stand the required burnup. The countercurrent method consists of moving blanket material from the outer portion of the reactor toward the center as the fissile content increases. Fresh blanket material is added at the outside of the reactor while spent fuel material is discharged at the center of the reactor. Thus, as the fissile content grows in any element of volume of the fuel, it is moved gradually into regions of higher statistical weight where its reactivity contribution becomes larger. It is only in a reactor with a substantial breeding gain that such a scheme becomes significant.

If the breeding ratio is not high enough, or if the fuel cannot stand the required burnup, supplementary fissile material ("spike") is introduced to maintain criticality. The fissile material in the core region thus consists partly of what was bred in the blanket material as it progressed toward the reactor center and partly of spike. The amount of the latter required becomes smaller the higher the buildup of fissile nuclides in the blanket. Thus, the amount of spike can be reduced both by raising the breeding rate and by allowing the blanket fuel to reside for a longer time in the reactor before it is removed. The latter measure also increases the burnup, however, and it is therefore limited by the burnup capability of the fuel.

It has been found that an ordered bed arrangement of fuel spheres is particularly well suited to the countercurrent fuel management scheme. Figure 1 shows graphically how an ordered bed assembly would be rearranged to obtain countercurrent fuel management. When the reactor builds up to equilibrium as shown on the left, each fuel as-

sembly is rearranged. Two layers of high burnup fuel are removed from the center of the assembly as shown in the center panel, and two fresh layers of fuel are added to the ends of the assembly so that a newly assembled element would appear as shown on the right-hand panel.

In the course of the reactor physics calculations, a general survey was first made to see what requirements must be met by the fuel if the entire budget of fissile material is to be furnished by the blanket - without any reprocessing or refabrication. These requirements can be expressed in terms of burnup and reactor height. Studies for U^{238} metal, carbide, and cermet fuels showed that even for rather tall reactors (i.e., low leakage and therefore high breeding rate) the burnup requirements for these fuels exceed their expected performance. Thus the fuels mentioned above would be required to sustain burnups respectively of 7, 11, and 19% in 4-ft-tall reactors. In the present case the cermet was assumed to consist of 80% by volume of UO_2 and 20% by volume of stainless steel.

The addition of fissile material to the reactor reduces the burnup which is required of the blanket fuel. This was studied in a number of reactor configurations with cermet fuels containing 60% by volume of UO_2 for the blanket and cermets containing various proportions of PuO_2 for the supplementary spiking material. With a 15% burnup limitation on the blanket fuel and a reactor height

Figure 1. Countercurrent refueling.

of 4 ft, the composition of the spike is the most important remaining variable. The breeding rate is improved by using a concentrated spike, i.e., by using a high Pu content in each spike ball. However, this increases the heat generation rate per ball, and a thermal limitation is encountered which is discussed elsewhere in this report. Hence several compositions have been under study. For each configuration the material balances as well as power peaking factors for spike and blanket balls have been established.

A number of additional calculations were performed to find critical configurations of ordered bed fuel elements that might be used in the Fermi and the SAFER reactors. M. LEVINE, A. ARONSON

SBR DYNAMICS

Using collapsed one-group cross sections and temperature coefficients, an analysis of the dynamics of the SBR under temperature perturbations was made using the NO MURK code. The core was mocked up by a six-region multipoint model; the end blankets and sodium plena were each considered as a separate region. In order to test practical stability at power, the equilibrium configuration was perturbed by arbitrarily imposing temperature distributions as much as 50% greater than the equilibrium values, and by following the resultant space-time transient. The results of such calculations show that the system is asymptotically stable. To test overshoot response, sudden and permanent drops in inlet temperature (up to 100°C) were imposed. These calculations showed that the maximum temperature power shoot reactor was limited to an increase of <25% over the original equilibrium values.

G. LELLOUCHE, M. LEVINE,
J. CHERNICK

Fuel Studies

FUEL PROCUREMENT

During the past year, the studies on carbide fuels were redirected toward 4 cermetes of UO_2 in stainless steel. The main reason for this change was the strong indications that a cermet may have the best chance of achieving the high burnup (>10 atom %) required of the fuel pellet. Earlier British work had indicated that a burnup of 10 atom % is attainable without serious distortion in 30 to 50 vol %

cermets. For the proposed OBR reactor a stainless steel cermet was chosen and the following preliminary specifications were established:

- (a) The matrix or metal phase shall be continuous.
- (b) The composition shall be 60 vol % fuel phase and 40 vol % metal phase. This represents the maximum fuel phase volume consistent with requirement (a) above.
- (c) The fuel phase particle shall be 400 μ to minimize recoil fission fragment damage to the matrix.
- (d) The matrix composition shall be such that no sticking will occur at the interparticle contact areas in liquid metal at the temperatures expected in the system.
- (e) Over-all particle density shall be 85% of the theoretical density, which represents a departure from the usual cermet fuel. The voidage ($\approx 15\%$) was specified to accommodate the swelling that is expected to result from the high burnup.

The pellets are not clad with any structural cladding but a thin ($\approx 30 \mu$) coating of matrix material is applied to prevent any fuel phase particles from entering the coolant stream. The low density specification which results in high porosity will allow the fission product gases to diffuse out, but the cladding will prevent the recoil fission fragments from entering the coolant stream.

The fabrication technique involves cold pressing and sintering, followed by coining. Typical stainless steel cermetes are shown in Figures 2 and 3. The UO_2 fuel particles appear to have cracked which is probably a result of the cold-pressing operation. The UO_2 particles are sintered to the final density prior to the compact pressing and sintering. Since the matrix phase is continuous and the pellet is

Table 1

Irradiation Schedule

Capsule No.	Start-up date	Removal date	Predicted burnup, atom %	Particle ΔT , °F
BNL-29-2	8/ 2/65	10/25/65	1.4	160
BNL-29-3	9/13/65	4/11/66	5.9	320
BNL-29-4	8/ 2/65	9/13/65	1.4	320
BNL-29-5	10/25/65	4/11/66	2.6	160
BNL-29-6	10/25/65	1/17/66	2.7	320
BNL-29-7	11/29/65	4/11/66	3.8	450

Burnup-Thermal Stress Relationships

Desired burnup, atom %	Predicted thermal stress, psi	
	Min	Max
1.4	8,000	14,500
1.4	16,500	29,000
2.6	8,000	14,500
2.7	16,500	29,000
3.8	45,500	79,000
5.9	16,500	29,000

Figure 2. 60 vol % UO₂-40 vol % SS cermet. 50X. Figure 3. 60 vol % UO₂-40 vol % SS cermet. 50X.

coated, this cracking does not appear to present any serious problem.

The availability of cermet fuels of 30 vol % PuO₂ in a metal matrix with the same specifications as the UO₂ fuel pellet has been investigated. These fuel pellets (designated spike pellets) are required in the present reactor design. In addition, the availability of fuel pellets of mixed oxides, UO₂-PuO₂, in a metal matrix was also investigated. These would simulate the blanket pellets into which the PuO₂ is bred. At present both types of fuels are available commercially. G. PANCER

IRRADIATION STUDIES

Pellets of 1/8 and 1/4-in.-diam UO₂-stainless steel cermet enriched to 20% U²³⁵ as well as depleted were purchased to be used for in-pile irradiations and out-of-pile control capsules, as well as general fuel property evaluation. The irradiations are being performed at the ETR and MTR in order to obtain the required high burnup in a reasonable time. The schedule for the irradiation of those specimens is summarized in Table 1. In addition, the expected operating conditions and desired burnup are also included.

The selected conditions for the irradiations are based on the need to know how the pellets will behave under different conditions of thermal stress and burnup. The thermal stress in the pellet, σ , can be calculated from

$$\sigma = K \frac{E\alpha}{1-\mu} \times \Delta T,$$

where

$$\Delta T = \frac{q''' r_o^2}{6k}$$

and

- k = thermal conductivity,
- E = Young's modulus,
- α = coefficient of thermal expansion,
- μ = Poisson's ratio,
- ΔT = temperature gradient,
- q''' = volumetric heat generation rate, and
- r_o = radius of sphere.

However, there is considerable variation in the limited amount of data available on these properties. Considering the spread in the data, the maximum and minimum stresses in the fuel in the various capsules at the desired burnup are tabulated in Table 2.

Internal stresses will build up as burnup increases because of the accumulation of fission gases. These stresses would be added to the nominal thermal stress. Further, the nominal thermal stress would change because of the change in the property values (E , α , k) as a result of fission damage. The rather limited capsule program was planned to yield the maximum amount of information with different burnup levels for each nominal thermal stress value over a range of burnups (short, intermediate, long) for the intermediate stress level (16,500 to 29,000 psi).

The irradiation capsule is similar to that used in the earlier UC irradiation tests conducted at the Brookhaven Graphite Research Reactor. The system uses the mixed gas annulus for temperature control with Ar and He gases. As in the previous capsules, a dead weight is used for interparticle loading. A radiograph of a typical fueled capsule is shown in Figure 4.

Duplicate capsules will be run out-of-pile under similar conditions of temperature, interparticle loading, and exposure time in order to differentiate between thermal and radiation effects. G. PANCER

FUEL- Na COMPATIBILITY STUDIES

The effect of loading on the sticking together of particles is being investigated in a series of out-of-pile tests. The test balls are subjected to loads similar to those in a full-size reactor in the presence of Na at the proposed reactor operating temperature. Initially, stainless steel ball bearings are being used, since their surfaces are similar to those in the oxide-SS cermet fuel balls. However, as soon as cermet fuels can be obtained, these will be tested.

Two screening runs were carried out in a test vessel containing a 6-lb batch of clean Na at 450° and 650°C, respectively. In each run, four ¼-in.-diam 316 SS balls were placed in a 316 SS block with single-point contact between adjacent balls. A load of 22 lb was applied to this column of four balls and maintained for the duration of the test. The assembly was fastened to the end of a stirrer whose rotation produced Na flow past the balls at velocities of ≈ 0.5 ft/sec. After 117 hr at 450°C and 24 hr at 650°C, the balls were removed and examined. No evidence of sintering at the points of contact was found. A tiny circular area on each ball (Figure 5), which measured ≈ 0.00003 to 0.00006 in.² and appeared flat under the microscope, was readily visible as a shiny spot and repre-

Figure 5. ¼-in.-diam 316 SS ball after exposure to Na at 650°C for 24 hr. Shiny spot at center of ball shows where adjacent ball contacted it at a loading of 22 lb.

sented regions in which plastic deformation (at a calculated stress of $\approx 5.4 \times 10^5$ psi) occurred at the points of contact between adjacent balls. No Na had penetrated these areas, so that it can be assumed that the balls were continuously loaded. It would have required a calculated force of 2.3 to 4.6 lb to pull two adjacent balls apart had sintering occurred before the individual balls could be removed and examined.

These studies were continued in small thermal convection loops which consist of a test column whose ends are welded to ½-in.-IPS piping to complete the flow circuit. The hot-trapped Na flows upward through an ordered packing of ball bearings at ≈ 0.1 ft/sec. The packing is heated with external resistance heaters and an external load is applied to the balls.

An 8-day run was completed with 304 SS balls under a total load of 222 lb (22.7-lb load on each point of contact) acting on a four-ball layer at 650°C. Some sintering occurred during the test, but considerable evidence was found that the external load was applied nonuniformly, so that both its magnitude and point of application on the individual balls varied and, in many cases, exceeded the calculated load. The test was run again but at 700°C with a total load of 113 lb (11.6-lb load on each point of contact), but results are not yet available. A third test is under way at 700°C and with an external load of 11.6 lb per contact point on oxidized 304 SS balls stacked with single-point contacts.

Figure 4. Radiograph of fueled capsule for ETR irradiation.

Subsequent tests will be conducted with other materials (e.g., 410 SS, chrome-plated steel, cermet fuels) at other temperatures, with different loads and various Na purities.

A small stainless steel pumped loop was assembled and filled with Na to permit an investigation of the effect of bed movement (i.e., ball on ball, and ball on container wall) caused by thermal cycling on the condition of the ball surfaces (e.g., attrition). The SS balls were packed in a cold-rolled steel column and relative bed motion was induced by changing the Na temperature.

The loop consists of a $2.76 \times 2.76 \times 36$ -in. test column attached to $\frac{1}{2}$ -in.-IPS piping. Na was pumped through a 6-in.-IPS surge tank downward through the test column with an electromagnetic pump at flows up to ≈ 10 gpm. The flow was measured with an electromagnetic flowmeter. The loop was provided with a cold trap and a means of suspending Zr foil in the surge tank. The Na was charged from an attached dump tank and can be sampled in both dump and surge tanks (i.e., during the run).

Na was circulated through the bed which was packed to a height of $18\frac{1}{2}$ in. with 11,270 0.250-in.-diam type 316 SS balls which were not externally loaded. The bed temperature is normally maintained at 290°C , and pure Na was heated periodically to 650°C in the surge tank and then circulated through the column at maximum pump velocity.

The test was terminated in October after a total of 560 hr of operation at Na temperatures between 125° and 650°C and 17 thermal cycles. The column has been radiographed several times, and the radiographs verified that a definite change in bed level occurred with thermal cycling without disordering the packing. H. SUSSKIND, W. BECKER

PELLET COATING

Work has been initiated on the coating of steel spheres with diffusion barriers to minimize possible sticking of the balls under load at 1200°F in the presence of Na and NaK. Because alumina is relatively unaffected by molten alkali metals at elevated temperatures, it might be considered to be a reasonable barrier layer for this purpose.

Several methods are being used to put an adherent layer of Al_2O_3 on stainless steel balls. These include the following.

1. Aluminum is evaporated uniformly onto $\frac{1}{4}$ -in. 304 SS balls in a vacuum plating system by rolling the balls about during the deposition. The coating however is quite thin (500μ). Attempts are now being made to apply thicker coatings by this method before diffusing aluminum into the stainless steel and oxidizing the surface alloy.

2. Stainless steel balls in a ZrO_2 boat are heated under an aluminum melt in vacuum. After building up a suitable diffusion layer, excess aluminum is to be removed by a dissolution and the surface alloy oxidized.

R. POWERS, J. KELSCH

THE INTERIM α - γ FACILITY

The construction phase of the facility is nearing completion and it is available for the installation of equipment in the α containment boxes. Equipment for the hot boxes can be set up when all power, water, and ventilation lines and manipulators have been installed. Figures 6 and 7 show shielding and containment boxes being put in place.

The interim α - γ facility is located in a room 21 ft $\times$ 55 ft in the Hot Laboratory building. The general layout is shown in Figure 8. The facility consists of three Argonne DDD type glove boxes, an inert gas welding dry box, and five shielded containment boxes. All the boxes, except the welding box, will operate with a nitrogen atmosphere in order to provide the maximum flexibility of the facility.

The three unshielded glove boxes are in most respects identical to the Argonne DDD boxes. Because only three boxes were required for this facility, it was more economical to use stainless steel frames than extruded aluminum members. The stainless steel is stronger than aluminum but lacks the rigidity of the heavier cross section of extruded aluminum. Supplementary reinforcing struts were required to prevent cracking of the glass panels and to permit proper tightening of the sealing gasket.

The welding dry box is 4 ft long and 3 ft in diameter. It is to be used for filling capsules with NaK and for making the final closure welds of capsules. The box can be evacuated and filled with purified Ar for welding. The Ar gas is purified by passing it over Ti-Zr chips heated to $\approx 800^\circ\text{C}$.

The shielded facility consists of five containment boxes fabricated with 11-gauge stainless steel. Four of the containment boxes are 3 ft wide, 5 ft long,

Figure 6. Photograph taken during construction and location of Argonne DDD boxes and metallography containment box.

Figure 7. The steel plate shielding for the large containment box.

and 4 ft high. Two of these will be used for chemical analysis and the other two for metallographic studies and physical measurements. The larger box is 5 ft wide, 10 ft long, and 5 ft high, and will be used for disassembly of irradiated capsules and compression testing of fuel pellets. All the boxes are interconnected with transfer tunnels.

The large containment box will be serviced with three junior-sized Model-8 manipulators. A pair of the manipulators are centered in front of the large window and a single manipulator is in front of the small window. Each of the four smaller containment boxes is equipped with a pair of through-the-roof Model-7 manipulators. All manipulators are booted gas tight and are removable from the cold side for maintenance. The bootings serve as contamination barriers. J. CHOW, A. BANSLABEN

The design and fabrication of the fission gas and capsule opening apparatus for the α facility is currently under way. This apparatus is the basic equipment necessary in order to perform the required pre- and postirradiation analysis of the cermet fuel specimen, and includes provisions to vacuum distill NaK rather than to react it with

alcohol. Alcohol treatment leaves a residue that alters the surface appearance of irradiated spheres. In this design a capsule is placed in a bakeable vacuum system, punctured by a pneumatic ram, and the fission gas removed to the collection system at room temperature. The NaK will then be vacuum distilled into a condenser at 450°C over a 6-hr period. A pipe cutter similar to that in the BNL Hot Lab cell has been adapted for remote operation to open the capsules and remove irradiated fuel pellets.

One of the more important means of characterizing fuel is by measuring its density before and after irradiation. Initial results of measuring UO_2 -Fe cermet pellets by three separate methods are shown in Table 3. For comparison, the resulting densities based on 100, 95, 90, or 85% theoretical densities of both UO_2 and Fe in compacts of this composition would be 10.03, 9.54, 9.02, or 8.52 g/cc, respectively.

On the basis of the above preliminary results the density values obtained on fuel appear to depend on the method of measurement. The mercury pycnometer gives the lowest density as would be ex-

Figure 8. Layout of alpha-gamma facility.

Table 3

Average Densities of 70% UO_2 -30% Fe Compacts

Method	Density, g/cc
Helium densitometer	9.763
CCl_4 displacement	9.468
Hg pycnometer	9.262

pected if no mercury penetrated the porous fuel pellet. The value of 9.26 g/cc obtained by this method is equivalent to an over-all pellet density 93% of theoretical. Carbon tetrachloride immersion results in partial penetration of the pores of the pellet, while helium densitometry results in the highest density because of complete penetration of interconnected porosity by helium.

A knowledge of the lowest density corresponding to the sample envelope (mercury immersion) and of the highest density (helium densitometer) should provide a measure of the interconnected porosity of the fuel. These two methods are being adapted for use in the α facility.

Because of the tedious nature of the initial measurements of density by a mercury vacuum pycnometer, it was decided that a more acceptable method for use in an α box and the hot cell would be that of mercury displacement. A tungsten sample holder has been constructed which can be immersed under mercury in a vacuum system to avoid bubble entrapment during the measurement. The system will be used in both the α box and in the hot box.

With a helium densitometer, an evacuated standard volume is isolated from a small volume measuring system containing pure helium at slightly below atmospheric pressure. When the standard volume is opened to the system, the pressure drops. Pressure is restored to its initial value by forcing an equal volume of mercury into the system. This volume is determined by measuring the weight of mercury in an attached flask before and after forcing it into the system.

In repeated measurements of one such standard volume (11 determinations) in a prototype apparatus, a value of 1.3449 ± 0.0067 cc ($\pm 0.5\%$) was obtained, while in another larger standard volume, a value of 2.8565 ± 0.0093 cc ($\pm 0.33\%$) was obtained. Since appreciable error can be introduced in such a system, if samples as small as 0.14 cc are measured, a second system (thermostated) has

been constructed with a modified standard volume. It is hoped that this new system, now under test, will show greater reproducibility with the small fuel pellets. This apparatus is to be used inside an α glove box while a sturdier version will be placed in the hot cell.

A helium permeability apparatus has been built for installation in an α glove box. Permeability will be measured on representative cermet fuels as an additional check on matrix porosity and of sample uniformity.

The fuel pellet is incorporated in an impervious plastic disc that is inserted between O-ring flanges in a vacuum system. After evacuation, one side of the disc is back-filled with pure helium at a known pressure, slightly above atmospheric. The volume of helium passing through the porous fuel sample is determined by measuring the exit helium from the vacuum pump by wet test meter. From the gas volume, pressure, collection time, and specimen dimensions, permeability is readily determined.

In early tests with the apparatus, a $\frac{1}{8}$ -in.-diam pellet of 60 vol % UO_2 -40 vol % 304 SS (coated and coined) was found to have a permeability of 4.1×10^{-3} cc/sec/cm²/mm thickness/cm Hg (helium). This compares with a value of 2.9×10^{-3} for a 70 vol % UO_2 -30 vol % Fe pellet. These values are in a direction that would be expected from their over-all densities of 7.0 and 9.3 g/cc, respectively. Negligible permeability was found for a $\frac{1}{8}$ -in. stainless steel rod briquetted in plastic and tested under similar conditions. A similar apparatus is to be built for use in the hot cell.

In the α facility sample dimensions are to be measured by an electronic micrometer. Handling jigs devised for use with fuel that is currently being irradiated (short cylinders with hemispherical ends) have proved to be satisfactory with the micrometer. Samples will be weighed on a single-pan analytical balance.

A small compression tester for use in the hot cell has been adapted for use with a manipulator. It will be used to test the loss of ductility of irradiated fuel at room temperature. A simple strain indicator is to be built for use with this apparatus.

Considerable reliance is to be placed on metallography for evaluating fuel performance. Metallographic equipment including that for sample preparation, viewing, and microhardness measurements is ready for installation. A remote stereoviewer has been purchased for macroexamination and photography of fuel. R. POWERS, S. JONES

Technology of Random Bed

STUDIES OF BED PACKING

The exact positions of spheres in packed beds provide useful data for the studies of settled and ordered bed reactor applications. A technique has been devised and partially explored for securing such data. This consists of embedding opaque markers at the centers of transparent spheres. The bed of spheres in which the measurement is to be made is filled with a liquid having the same index of refraction as that of the marked spheres. This makes the spheres themselves invisible, only the markers at their centers remaining visible. Then measurement of the coordinates of these markers in front and side views provides the necessary data.

Such measurements have been made on the optical comparator of the Machine Shops Division. The distribution of sphere centers in a small bed containing 45 marked spheres was measured. The radial distribution function from these data was found to be consistent with results reported in the literature.

Some of the difficulties encountered in going to beds with thousands of spheres are:

(1) Obtaining spheres with markers that are well-centered; many marked spheres have had to be rejected.

(2) Obtaining a good match in refractive index between spheres and the liquid used to fill the bed becomes more and more important as the size of the bed is increased. Several liquids appear promising but additional work remains to be done.

(3) The measurement process must be speeded up. The optical comparator is not too well suited to the job because the measuring process is slow, and the many manipulations of the bed during the long period of measurement tend to make it shift. Preliminary efforts at measurements from photographs have been promising. With the use of a camera setup of the Bubble Chamber Group, it was possible to produce photographs which can be scanned on the measuring instruments used for bubble chamber films. Additional work is needed to establish how well this method will work.

J. CHERNICK, M. LEVINE, W. BECKER

A numerical model of random packing of hard spheres has been studied by means of a computer program. A cell is constructed by allowing as many spheres as possible to be tangent to a given sphere at random positions. Many such cells were con-

Figure 9. Response to one 12-g shock.

structed and the statistics of the number of neighbors and of the cell volume were observed.

J. CHERNICK, M. LEVINE

The equation of state of a collection of hard spheres in a spherical container has been investigated with the aid of the computer. This work indicates a change in phase near the packing density corresponding to about 64% solid fraction. This work is not yet complete.

M. LEVINE

BED STABILITY

To establish a point of reference in bed stability, a randomly packed bed is considered stable if a 12-g lateral shock could not produce more than a 10% reactivity increase. By this definition, beds settled from a state of fluidization without some initial compaction were found to be unstable. Consequently, it was necessary to develop a practical means for compacting a bed before the test of stability would be meaningful. For this purpose, hydraulic pulsing was used to impart very small amplitude up-and-down motions to the beds, which permitted some local repositioning of particles and resulted in the formation of more compact and more stable beds. Bed stability was found to increase sharply with compaction and, thus, only short periods of pulsing were necessary.

Previously, a means for measuring very small changes in packed bed solid portion (a membrane cap) had been developed [see BNL 900 (S-67)].

The effect of a 12-g lateral shock on the solid fraction of beds which had been hydraulically pulsed was studied using the membrane cap.

The experimental results (Figure 9) show that beds settled from fluidization can be remotely compacted by hydraulic pulsing to exhibit, as the result of a 12-g lateral shock, a change in solid fraction of about $\frac{1}{2}$ of the acceptable change discussed above. Furthermore, it should be noted that the particle interlocking effect of simulated coolant downflow gives a substantial extra measure of stability. The proposed reactor concept will have a pressure drop gradient of ≈ 10 psi/in. Although the experiments dealt with beds no larger than 6 in. in diameter, it is considered that the problems of scale-up with respect to bed stability alone could be approached with confidence.

R. PARSICK, S. JONES

PACKING NONUNIFORMITY

Nonuniformity of solid fraction of randomly packed beds will cause a corresponding nonuniformity of coolant distribution. To evaluate the consequence of having a small region of packing denser than the average requires a knowledge of its location with respect to the reactor heat generation distribution. If the denser packing occurred near the external wall of the reactor in a region with a local-to-average power generation of < 1.0 , the coolant velocity decrease due to the denser packing could be compatible with the heat generation and, in fact, could produce a more uniform reactor outlet temperature than for uniform coolant flow.

To examine solid fraction distribution, a prepared 6-in.-diam $\times$ 5-in.-high bed of $\frac{1}{8}$ -in. brass spheres was "solidified" with epoxy resin and cut into five horizontal layers, each of them being further subdivided into 32 cubes each ≈ 1 in.³ in volume. For each cube, the volume was determined pycnometrically, the epoxy resin removed by molten NaNO_3 , and then the sphere volume measured.

The data showed a variation in the average solid fraction of the five horizontal layers of the bed. This variation from layer to layer does not represent a hot-spot problem, since all the flow passing through one layer by continuity passes through all layers, although it would have a minor effect on pressure drop. However, the solid fraction of the top one-fifth of the bed was 0.60 compared to 0.64 for the remainder. This might mean that the top of the bed is more susceptible to further consolidation than the bed as a whole. Stability studies using the

membrane cap measured the total change in bed solid fraction. If that change occurred primarily in the top $\frac{1}{5}$ of the core, the core reactivity increase would be less than if the solid fraction change occurred uniformly throughout the bed. This reduced effect results from a local-to-average worth of < 1 for the top $\frac{1}{5}$ of the core.

The data also indicate that above average solid fractions within the bed occur closer to the container wall than to the bed center (see Figures 10 and 11). Data from a second "solidified" bed showed slightly less radial and axial variation (see Figures 12 and 13). Both beds had an average solid fraction of 0.635 and the top 20% of each bed was looser than that of the remainder.

Meaningful measurements of fluid velocity even at the exit of a packed bed is difficult. Specially designed bed support grid and pitot tubes were used to explore the variations in fluid velocity at the outlet of hydraulically pulsed 6-in.-diam beds containing $\frac{1}{8}$ -in. polished SS spheres. At a Reynolds number of 1000, the minimum-to-average flow velocity at the bed outlet was about 0.8, and occurred ≈ 2.0 in. from the central axis of the 3.0-in.-diam bed.

R. PARSICK, S. JONES

Technology of Ordered Beds

REMOVAL OF SPHERES FROM AN ORDERED PACKED BED

Studies were carried out on the removal of individual layers of balls from the top of an ordered packed bed without disturbing the remaining packing. This procedure could be utilized in the countercurrent fuel movement for the ordered bed fast reactor. Three techniques were successfully applied: the use of (1) fluid jets which are discussed in more detail below, (2) an inverted funnel head, and (3) a piston lift.

The inverted funnel head is a movable device which is lowered into the packed column and positioned above the bed surface. Liquid flows downward along channels in the periphery, exiting through slits at the bottom. The balls along the bed surface are thereby fluidized and removed directly through the funnel cavity.

In the third technique the entire bed is lifted in piston-like fashion. Fluidizing liquid provides the required lifting force by pushing against a movable support plate on which the entire bed is packed.

* NONLINEAR SCALE APPROXIMATES RELATIVE DISTANCE OF CENTER OF SUBDIVISION FROM CENTER OF BED.

Figure 10. Solid fraction within a randomly packed bed - I.

* NONLINEAR SCALE APPROXIMATES RELATIVE DISTANCE BETWEEN CENTER OF SUBDIVISION AND CENTER OF BED.

Figure 12. Solid fraction within a randomly packed bed - II.

Figure 13. Solid fraction distribution for a pulsed bed of 0.6350 solid fraction - II.

As the top layers of the bed reach the top of the packed column, liquid flowing out of a slit on one side lifts them and sweeps them through another slit on the opposite wall.

In considering the use of fluid jets it was observed experimentally that liquid entering two opposite sides of a column above the surface of an ordered packed bed of balls through rectangular nozzles could remove selectively individual ball layers from the top of the bed without disturbing the remaining packing (Figure 14). The depth of bed penetration increased with higher flow rates through the nozzles. A wide range of variables was investigated and a general correlation found. A model of this complex flow system was also postulated.

The experiments were conducted in two square Lucite columns, 1.795 and 3.725 in. on each side, respectively. A series of paired rectangular nozzles was machined along two opposite sides of the columns which were either $\frac{1}{16}$ or $\frac{1}{8}$ in. wide, spanned the entire width of the column walls, and were inclined upward at angles varying between 30° and 90° from the vertical. Each pair of nozzles was located at a different height in the columns and those not in use were sealed with brass plates. The beds were packed in an ordered array on a flat Lucite plate provided with suitably spaced countersunk depressions.

The bed packings consisted of 0.125, 0.250, and 0.500-in.-diam stainless steel, aluminum, and nylon balls.

Water was circulated by a centrifugal pump from a surge-supply tank through copper tubing that was connected to the various column nozzles with heavy-duty flexible rubber hose. The flow rate was controlled with a manually operated throttling valve and pump bypass circuit, and measured with a previously calibrated rotameter. The entrained balls were collected in an overhead Lucite classifier from whence they could be returned to the column again through a ball valve.

Flow patterns in the column were studied with red dye injections in conjunction with high-speed (1000 frames/sec) movie photography.

Ducted turbulent jets are formed by the liquid entering a relatively stagnant fluid and form vortices underneath the jets. The two initial vortices, in turn, generate a chain of vortex pairs down into the column, their energy decreasing with distance from the nozzles. These chains may be considered as energy transmission linkages whose length de-

Figure 14. Lucite column (1.8×1.8 in.) packed with $\frac{1}{4}$ -in.-diam SS balls showing the removal of the top bed layers with water flowing through $2\frac{1}{2}$ -in.-thick nozzles inclined 70° with the vertical.

depends primarily upon the energy imparted by the fluid jets to the first vortex pair, and the extent of the viscous damping losses in the relatively stagnant fluid. The horizontal component of the lowest vortex in the chain helps to entrain the balls on the bed surface. The balls are then transported upward through the series of progressively more energetic vortices, receiving additional energy when moving past the fluid jets, until they have gained enough momentum to leave the column overhead with the exiting liquid.

The data could be correlated within $\pm 10\%$ by

$$x = 14.5 \exp(1.08P),$$

where

$$x = \frac{V_c V_j \cos^2(\phi/2)}{V_p^2 \sqrt{A_j/2A_c}}$$

and where

Figure 15. Correlation of liquid flow through nozzles in a packed column with penetration of the ordered packed bed.

V_c = average fluid velocity in column,
 V_j = average fluid velocity in nozzle,
 V_p = terminal velocity of single sphere,
 A_c = column area,
 A_j = nozzle area,
 ϕ = inclination of nozzle with vertical, and
 P = ratio of distance between nozzle and bed surface to column width.

The results are plotted in Figure 15.

H. SUSSKIND, M. MARESCA,
 R. ODETTE, W. BECKER

FUEL SORTING

A schematic flow sheet was made up on the assumption that each fuel ball discharged from the reactor would be separately examined (automatically), and that on the basis of the observed radioactivity the balls would be sorted and later poured

Figure 16. Stainless steel column (11×11×30-in.) used for tests to measure the pressure drop through ordered packed beds. Lucite windows on the sides permit viewing of bed structure.

into the reactor in the sequence necessary to give the desired distribution of plutonium. All operations in the cycle (i.e., everything except processing and fuel fabrication) would be done in a closed system under liquid sodium.

It was concluded that such a system is feasible and not too expensive. Development would be required but appears to be straightforward. F. MILES

PRESSURE DROP STUDIES

The pressure drop through large ordered packed beds of spheres is being measured in the 1000-gpm water test loop which was modified to incorporate an $11 \times 11 \times 30$ -in. test column (Figure 16) and testing has recently been initiated. The effect of the following variables will be studied: water velocity (0 to 1000 gpm), sphere size ($\frac{1}{8}$ to $\frac{1}{2}$ -in.-diam), bed voidage (0.26 to 0.32), spacing between adjacent balls (1.00 to 1.22 ball diameters), and bed height (0 to 24 in.). It will be possible to separate the effects of voidage and ball spacing (i.e., the size of the open flow channels) in these tests. Furthermore, the use of different sized balls in the same column will permit a measurement of the effect of the container walls. The bed entrance and exit effects will be measured by varying the bed height.

H. SUSSKIND, M. MARESCA, W. BECKER

Design and Evaluation

A conceptual design and cost estimate is being prepared for a 1000-MW(e) ordered bed fast reactor using countercurrent fuel management. This study will cover reactor physics, mechanical design, thermal and hydraulic design, fuel handling, and economics. Because of favorable results from various radiation tests by cermet fuel, it is expected

that higher burnups will be obtainable from cermet spheres and that the fuel cycle costs will be considerably lower than that of other rod-type fast reactors that are now in current favor.

M. LEVINE, A. ARONSON, L. GREEN, L. EPEL,
G. NUGENT, R. PARSICK, H. SUSSKIND

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Reactor Physics Division

J. CHERNICK, H. KOUTS

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N. CORNGOLD

NEUTRON THERMALIZATION

The exciting developments in the theory of pulsed neutron physics which characterized our research in 1963-64 were present again in the first part of 1964-65. They were succeeded by a period of summing-up. At present, research is aimed at elucidating, through detailed analysis of special models, several points of theory which are poorly understood by workers in the field.

An important contribution of the past year was a paper on the discrete relaxation times in thermalization. This paper was a summing-up of the theory of time-dependent thermalization in systems which are not too small. It dealt particularly with the dependence of eigenvalue spectrum upon moderator-type, and provided an explanation for the striking numerical results found in earlier research.

The recent analysis was based upon two ideas, the trick used by Lehner and Wing to analyze the spectrum of eigenvalues in the one-speed problem, and the Van Hove formalism for describing the scattering of thermal neutrons by moderators. With the use of these tools, it was found that the nature of the discrete spectrum (i.e., the decay constants observed in experiment) is closely correlated with the ability of the scattering atom to diffuse during long intervals of time. In the case of a crystalline solid, where an atom is confined to a region of space close to a lattice point, the discrete spectrum is almost empty. On the other hand, a perfect gas moderator produces a very dense set of discrete eigenvalues. The liquid moderator is, in a sense, intermediate, although the possibility of diffusion to points arbitrarily distant causes the discrete spectrum to resemble most the gas spectrum. In all cases, the discrete spectrum is augmented by a continuous spectrum which exists over portions of the line $\lambda > \lambda^* \equiv (\nu\Sigma)_{\min}$. It should be mentioned that the recent experiments of Starr, and of Kallfelz and Reichardt, which are con-

cerned with crystalline moderators, yield results not inconsistent with the BNL predictions.

Once the correlation of discrete spectrum with moderator type is understood, it is not difficult to take effects of absorption, and leakage, into account. These agents will attenuate the discrete spectrum, and in some cases can cause it to disappear altogether. In any event, one cannot have a proper discrete mode with $\lambda > \lambda^*$. Yet such values have been reported in the literature, and have been justified by analysis based upon a Boltzmann equation with truncated scale of velocities. However, simple considerations show that the truncation is quite unnecessary, and that the conventional theory can explain the experiments quite satisfactorily. These arguments were sketched in a recent published note, and are being subjected to quantitative analysis.

A discussion of the BNL research sketched above formed the main part of a survey paper presented at a recent IAEA symposium. Two aspects of the theory which remain unclear are the $\lambda > \lambda^*$ modes, and the dependence of λ upon size in very small samples. The first topic is connected with the fluctuating behavior of scattering cross sections in crystalline moderators. The second is, in essence, a problem in transport theory. Both are under investigation at present. In the latter, the multi-speed transport equation in slabs and spheres has been solved, to obtain time eigenvalues which range from zero to λ^* . The principal approximation lies in the form of scattering kernel, which is taken to be a separable kernel.

Several years ago, M.M.R. Williams solved the multispeed Milne problem for an absorption-free moderator whose scattering was described by a separable kernel. The class of solutions generated by Williams greatly resembled the class of numerical solutions obtained by C. Eisenhauer for the corresponding exact kernels. Thus, the separable kernel has more than academic value. During the past year, Williams' solution has been generalized to include absorption laws of the form $1/\nu^n$. The new solutions give emergent spectra, extrapolation lengths, and diffusion lengths as a function of ab-

sorber-concentration, and yield insight into experimental data on leakage spectra, which are beginning to appear in the literature.

The dependence of diffusion length upon type of absorption law may be studied in detail when the scattering kernel is simple. It is also possible to make statements about the diffusion length in the general case. This is the subject of the maximum absorption theorem, which asserts that for a large class of absorption laws, the diffusion length exists only for a limited range of concentrations. A crude proof of the theorem was published in 1964; a refined version of the proof will soon appear. Also, a critique of the use of diffusion theory – in several papers published recently – to calculate diffusion lengths in crystalline media will soon be published.

A paper has been published in which the effect of spin correlations upon the slow neutron cross section of methane is examined. It is found that the restrictions placed upon the proton-spin states by the Exclusion Principle can be ignored in experiments performed at room temperature. These results are particularly relevant to the analysis of scattering law experiments performed at the MTR.

Finally, a paper discussing a rather general aspect of reactor theory, the definition of reactivity, was presented to the American Nuclear Society. In the paper, it is pointed out that the experimental prescriptions given by Sjöstrand and Garelis and Russell lead to different definitions when multivelocity and transport effects are taken into account.

N. CORNGOLD, I. KUSCER, C. SHAPIRO,
K. DURGUN, J. DORNING, J. ARKUSZEWSKI,
P. MICHAEL

NEUTRON TRANSPORT IN FAST AND INTERMEDIATE SYSTEMS

A computational study of the diffusion of fast neutrons in materials that are found in fast systems has begun. The studies are aimed at testing our present knowledge of cross sections and the accuracy of the more popular approximations to transport theory. It is hoped that they will also suggest experiments whose results will provide sharp tests for the popular means of computation. A comparison has been carried out of the several computational recipes for fast systems. The discussion of criticality searches, spectrum indices, and sodium and Doppler coefficients was presented at a recent ANL meeting on fast reactor physics.

A. ARONSON, P. MICHAEL, M. LEVINE

The conventional treatment of slowing down in the moderator has been improved by treating that process by the IR (intermediate resonance) rather than the NR (narrow resonance) approximation. The new treatment greatly improves the agreement between "analytical" resonance integrals and those determined by Monte Carlo calculation. The older treatment, as exemplified by the ZUT code, could produce an absorption in the 6.7-eV resonance in error by 30% in a graphite-moderated lattice. The error is reduced to 6% through use of the IR.

R. GOLDSTEIN, B. SEHGAL,
A. ARONSON

REACTOR KINETICS

Considerable effort was spent in 1964-65 on the analysis of stable, periodic solutions to the (non-linear) kinetics equations. Research was completed on the subject of centers and limit cycles in reactor kinetics and on the subject of power oscillations in reactors with linear feedback.

The work on limit cycles extends and applies a technique used by Krylov and Bogoliubov. With it, one can analyze the complex frequency when a smallness parameter, introduced to generate a series, is "of the order of unity." The frequency of limit cycles in the Xe problem and in the motion described by the van der Pol equation has been computed and close agreement with machine calculations has been found.

Other research is concerned with the response function (describing function) and periodic solutions in reactors having arbitrary linear feedback and no delayed neutrons. What is novel about the analysis is the treatment of the amplitude of the first harmonic in the Fourier expansion of the logarithm of the power. The amplitude is treated exactly, without recourse to a linear approximation. For ease in calculation, however, amplitudes of higher harmonics are assumed to be small.

The problem of stability received considerable attention from summer associates of the Reactor Physics Theoretical Group. Two criteria were derived in terms of integral properties of the feedback kernel, which ensure boundedness of all solutions of kinetic equations having a linear feedback mechanism. One also considered reactor systems with time delays due to convection and applied to them, with success, general stability methods devised by the Russian mathematician, Pontriagin.

L. SHOTKIN, A. AKCASU, H. JACOBOWITZ

Space Dependent Kinetics

A reactor kinetics code which solves the space dependent nonlinear one-group diffusion equation in slab geometry in ten regions with up to 500 space points has been prepared and tentatively dubbed NO MURK. The code contains provision for using a flowing coolant and up to ten delayed neutron groups in each region. Various perturbation and output routines are available. The code is in limited production use at the present time.

Nonlinear Stability Theory

By noting the invariance of the space independent reactor kinetics equations under nonsingular linear transformations, it was possible to recast the usual canonically formulated asymptotic stability criteria into terms of the physical parameters. This permits the establishment of design inequalities which are directly applicable to the qualitative study of design stability. It also permits the determination of the qualitative aspects of varying of the physical parameters. For example, it was found that, for the two temperature feedback system, delayed positive and prompt negative physical reactivity coefficients always led to asymptotic stability in the large as long as a power equilibrium state existed. The same is certainly not always true if the delayed coefficient is negative. Similar results were found for the three temperature model.

Extended Nonlinear Stability

Welton's criterion for nonlinear stability in the large is known to yield a smaller region of parameter space than does Popov's criterion. It is an open question as to whether Popov's criterion covers the same region of parameter space (except possibly for boundaries) as does the linear criterion for asymptotic stability at all power levels. We have shown that certain necessary conditions that this be so are indeed satisfied, and that in particular the model containing three temperature feedbacks is asymptotically stable in the large whenever it is so in the small at all power levels.

G. LELLOUCHE

FLUID DYNAMICS

After completing and publishing studies of the flow of an ideal fluid parallel to a line of spheres,

a second problem, the flow of a viscous, incompressible fluid past a disc, was analyzed. In an early study, the boundary conditions at infinity were treated by considering the flow past an infinite sequence of discs, as their separation increased. This method was found to be inferior, however, to the direct imposition of the conditions, combined with a mesh size which increased exponentially with distance from the disc. Other specialized numerical techniques were required before final, converged results were obtained. These gave values of the drag coefficient, as a function of Reynolds number in the range $1 \leq Re \leq 60$. The agreement with experiment was excellent. In connection with this research, the convergence of various iterative schemes for the solution of the Navier-Stokes equations was analyzed. The approach was based upon the eigenvalue spectrum of the difference equation.

P. MICHAEL, D. GOLDER

PACKING OF HARD SPHERES

The difficult and intriguing question of the stable configurations of a system of hard spheres, randomly packed in a container, is being answered by computer research. Two distinct computing strategies have been used in trying to solve what is essentially an N -body problem. Both require that the spheres enter the container one by one, and that the positions of earlier arrivals are known. In the first, the new sphere is placed in the position of minimum potential energy, while in the second, subregions of phase space are chosen at random, and the sphere is placed in a local minimum, within the subregion, if one exists. Working with $\approx 10,000$ spheres, it is found that the first scheme gives void fractions within the range of experiment, and that the second – as one might expect – produces packings somewhat “looser” than the observed. The computer experiments, when completed, will provide an immense amount of numerical data about the packings. In particular, one will know the local void fractions and local variations of coordination number, both quantities of considerable physical interest.

B. CLANCY

Sphere Assemblage Simulation

SAS, a computer program designed to simulate packing of spheres, has been successfully tested. The first 41 spheres formed a grid on the bottom of the container. Additional spheres, with random

x and y initial coordinates, were added until the total number of spheres was 810. The resultant bed was perfectly ordered with no holes.

By allowing spheres to roll down a succession of spheres, the program gives a realistic distribution of accessible spheres and promotes a closer packing. For example, the 810 spheres, if leveled off, would form 20 layers (10 of 41 and 10 of 40); the program completed the 19th layer and placed 31, 8, and 1 in the 20th, 21st, and 22nd layers, respectively.

In the ordered bed, all spheres in a given layer should have the same z coordinate and should lie directly above those two layers below. Although there is a small round-off error in each calculation, the computation is very stable. The *maximum range* in the z coordinate of spheres in a given level was < 3 parts in 10,000,000. The *maximum displacement* from the x or y value of the original grid position was $\approx 2 \times 10^{-6}$ ball diameter. Average computing time was 1.8 sec/sphere.

The program features cutoffs and rapid sorts. Detailed calculations are limited to a few spheres in the bed. Answers are generally obtained from explicit algebraic expressions; a few special cases use very rapidly convergent iteration. All routines are single precision.

Once a sphere has been added, it continues to fall and/or roll until it is completely supported. Provision is made for cases in which a ball falls off another, or is supported by only one of two spheres, or one or two of three. A recent innovation is the inclusion of stability parameters. Although a sphere is supported by three others, it may be in a precarious position with respect to those spheres. If the program finds this to be the case, it searches for additional support in the form of a wall or another sphere. If none exists, the sphere rolls over the unsupported side and continues its journey.

A recently added cutoff has made the speed of the program virtually independent of the number of spheres in lower layers. Also, the speed is only slightly affected by the number of spheres in a layer. Thus it appears feasible to build up a cluster of 5000 spheres in $2\frac{1}{2}$ to 3 hr of computing time. Larger clusters are possible because computer memory can be conserved by "retiring" spheres in lower levels and retaining only those which could conceivably be contacted by incoming spheres. The program has an interrupt feature which enables it to be done in several stages if desired.

E. TORV

Reactor Physics Analytical Group

R. HELLENS

THEORETICAL STUDIES

Resonance Absorption Theory for Heavy Moderators

An extensive effort was made to remove the usual narrow resonance approximation for the moderator in reactor systems. Studies were made through the intermediate resonance theory wherein parameters were introduced for all the species present in the system. Methods were developed for calculating these parameters in both homogeneous and heterogeneous systems. The calculation of the Dancoff factor in the heterogeneous lattices was modified to account for the intermediate nature of the scattering removal process of the outside moderator.

The intermediate resonance method was compared with Monte Carlo calculations for a variety of systems and resonances, and it was found that there was very good agreement between the two methods. The study shows that the narrow resonance approximation for the moderator is not valid for the low lying wide resonances of absorbers like U and Pu, and large discrepancies in resonance integrals may be introduced for systems moderated with Be and carbon.

Doppler coefficients calculated by the intermediate resonance methods are generally in agreement with the Monte Carlo calculations. Equivalences among homogeneous systems and among heterogeneous systems are established through the intermediate parameters.

B. SEHGAL

Neutron Transport in Slab Arrays

A study has been made by numerical methods of the anisotropy of thermal neutron transport in slab lattices. The neutron scattering was taken to include linearly anisotropic terms and S_n methods were used to compute the kernels required in the two-dimensional solution of the integral transport equation. Calculations were performed for a series of Al-H₂O slab lattices which are now being studied experimentally at BNL. The results indicate that a substantial anisotropy in the thermal neutron diffusion exists. H. HONECK, B. QUIQUEMELLE

Resonance Capture in Clustered Lattices

The conventional theory of resonance capture has been extended to clustered lattices in which

the slowing down of neutrons within the cluster must be distinguished from that in the surrounding moderator. Exact solutions have been obtained only for the case of square resonances with hydrogen moderation but from these results an approximate expression for the capture of resonances of arbitrary line shape can be inferred. The escape probability is found to be identical with the narrow resonance approximation through terms linear in the resonance width, but in general the resonance integral inferred from the present formula will be somewhat smaller than the conventional result. This decrease in capture can be interpreted as a source depression effect in the cluster. Expressions for the various cluster collision probabilities have been derived which show that the Dancoff factor for a cluster is related to that of an infinite lattice through a single variable which depends principally on the number and geometrical arrangement of the absorber rods in the cluster.

R. HELLENS

Effect of Fuel Cladding on the Dancoff Factor

A simple analytical approximation to account for the effect of fuel cladding on the Dancoff factor in heterogeneous lattices has been developed. Comparisons of this method with Monte Carlo calculations show excellent agreement.

It was found that the presence of the cladding can significantly change the Dancoff factor, and consequently the resonance capture, in a tight lattice.

B. SEHGAL

Neutron Thermalization Theory

The effect of a nonuniform temperature distribution on the stationary thermal neutron distribution was studied in an extended nonabsorbing, nonisothermal moderator. Expressions were derived for the neutron concentration diffusion coefficient and the neutron thermal diffusion factor for the special cases of a hydrogen gas moderator and a heavy gas moderator. The results were compared with previous studies.

B. SEHGAL

ANALYSIS OF LATTICE MEASUREMENTS

Th²³²O₂-U²³³O₂ Fuel

The analysis of Th²³²O₂-U²³³O₂ lattices was continued and some effort has been devoted to D₂O moderated lattices with the aim of designing future experiments. Studies of the Th²³² resonance integral were continued in evaluating the new res-

onance parameter data of Th²³² from General Atomic and Harwell. The effect of interference scattering between the two lowest resonances of Th²³² on the resonance integral is being studied. A review of all the pertinent cross section data is being made prior to starting final calculations for the lattices measured at BNL.

Graphite Moderated, U²³⁵-Fueled Assemblies

A preliminary analysis of the minimum reflection U²³⁵ graphite lattice experiments has been completed. Spectrum and criticality calculations were done with the HAMMER code while some detailed calculations were made for resonance capture by the REPETITIOUS code and for the fast fission and leakage by the MOCA-2A code. The results for k_{eff} and critical buckling show excellent agreement with the experimental results.

Pu-Al Fuel

A series of MUFT-THERMOS calculations was done for the proposed Pu-Al-fueled D₂O-moderated lattices covering D₂O/fuel volume ratios of 2 to 20 and boron concentrations of 0 to 15 g/liter of B₂O₃. The rods are 0.6 in. in diam with 10% Pu by weight (of which 8% is Pu²⁴⁰). The calculations indicate that a sufficient fraction of epithermal fissions is obtainable with moderate B₂O₃ concentrations (<10 g/liter) and practical volume ratios.

Several series of support calculations were done to help the experimental group in designing experiments on cluster fuels, anisotropic migration, and cadmium ratios.

H. CONNELL, H. HONECK,
B. SEHGAL

DEVELOPMENT OF LATTICE ANALYSIS CODES

A considerable effort this year was made in developing, testing, and checking out of the HAMMER code. This combines and improves the codes MUFT, THERMOS, ZUT, TUZ, and FOG into a single lattice spectrum and criticality code which is particularly designed for the analysis of exponential experiments. The programming of HAMMER was greatly aided by the collaboration of Dr. John Suich of the Savannah River Laboratory. As a check of the over-all HAMMER system, the analysis of UO₂-H₂O lattice experiments has been repeated and the results indicate good agreement with both the experimental data and the previous calculations.

H. HONECK

Extensive modifications have been made in the fast neutron spectrum code MOCA-2 for the IBM

7094 computer. The code as it now stands provides Monte Carlo estimates of fast fission, absorption, flux spectrum, moments of the slowing-down distribution, etc., in a heterogeneous reactor lattice. This work has been carried out in collaboration with R. Dannells of the Westinghouse Atomic Power Department and a report (WCAP-2685) has been issued.

H. HONECK

A resonance integral code was developed for homogeneous systems to do an exact numerical integration of the slowing-down equations while taking into account all the resonance levels present. This will afford calculations that estimate the effect of Placzek oscillations in the flux and any interference between individual resonance levels. The code has been partially checked out.

S. BEAN, H. CONNELL

A multipurpose S_n code was developed for the computation of transport kernels in slab and cylindrical geometries in which the source of neutrons and the cross sections can be angular dependent. In addition, the conditions at a cell boundary can be any kind of combination between mirror reflection and isotropic scattering.

The numerical solution of the flux equations was coded only in the case of slab lattices.

B. QUIQUEMELLE

Reactor Physics Critical Facility

G. PRICE

Minimum Reflection Critical Facility

In this facility, a series of critical experiments with graphite-moderated cores using highly enriched U^{235} fuel is being carried out.

The cores being investigated are parallelepipeds and are bare; in fact, steps have been taken to reduce reflection to a minimum. Assemblies are elevated about 20 ft above ground level and are supported and contained by structures made almost entirely of aluminum.

The purpose of the experiments is to find precise critical masses of mixtures which are relatively homogeneous, and concomitantly, to measure parameters the value of which is useful in theoretical calculations or interesting for comparison of theory and experiment. Quantities of this nature include buckling, disadvantage factor, prompt neutron generation time, temperature coefficient, and spectral indices. Additional measurements are done for safety (as, for example, the reflector worth

of a man near the assembly as approximated by a column of water), or to find the proper factors pursuant to correcting the critical mass for existing structural reflection, control rod follower perturbation, and so forth.

In the course of the experiments, nominal graphite-to- U^{235} atom ratios thus far have ranged from 23,000 to 950. Six assemblies have been constructed; one of these was a repeat of the first, which was rebuilt to include more extensive and more precise measurements using techniques worked out as the experiments progressed.

During the present year, the repeat assembly designated Assembly No. 5, was brought critical. Assembly No. 5 had four graphite bars per fuel strip with a nominal graphite-to- U^{235} atom ratio of 22,900:1 and a total U^{235} content of 7.9 kg. While there is some slight overlap in reporting (1 or 2 of the following measurements was made during a prior report period), experiments on this assembly included measurement of temperature coefficient of reactivity, neutron reflection, rod sheath and follower perturbation, and spectral indices.

Upon completion of the measurements, Assembly No. 5 was dismantled. During the interim prior to building a new assembly, a battery powered electric drive (fast mode) was installed in the facility in place of an air motor drive. The operation of this system was checked and adjudged acceptable, after which the experimental program was continued.

The next assembly, which was designated Assembly No. 6, was constructed using a different and more concentrated uranium-aluminum fuel than was used in earlier assemblies. Although it is not convenient with this fuel to correlate fuel strips with graphite bars, one thickness of the new fuel was associated with one graphite bar. Since the concentration of uranium per unit area in the new fuel is about five times that of the old fuel, this assembly has roughly five times the uranium concentration of the most concentrated prior assembly. The nominal carbon-to- U^{235} atom ratio is 950:1. The nominal assembly dimensions are $39 \times 40 \times 72$ in. and the critical mass is 60 kg of U^{235} .

Parametric measurements proposed for Assembly No. 6 are those outlined above and performed on earlier assemblies. Two of these measurements, namely, buckling and neutron return, have been largely completed. Table 1 gives some results. These data are preliminary in the sense that they have not been formally published and are subject

Table 1
Some Minimum Reflection Critical Facility Results

	C/U ²³⁵ , atom ratio	$B^2 \times 10^4$, cm ⁻²	$\bar{\Psi}_{\text{fuel}}/\bar{\Psi}_{\text{moderator}}$	l^*/β , sec	$-\Delta\rho/\Delta T$, $\phi/^\circ\text{C}$
<u>Assembly No. 1</u>					
Calculated	22,900	9.40	0.945	0.177	—
Experimental	22,910	9.100 ± 0.1	0.941 ± 0.005	0.173 ± 0.003	4.51
<u>Assembly No. 2</u>					
Calculated	17,200	11.08	0.939	0.137	—
Experimental	17,180	10.98 ± 0.05	0.949 ± 0.006	0.143 ± 0.003	3.98 ± 0.26
<u>Assembly No. 3</u>					
Calculated	11,450	13.45	0.949	0.947	—
Experimental	11,450	13.40 ± 0.05	0.953 ± 0.006	0.099 ± 0.002	2.70 ± 0.28
<u>Assembly No. 4</u>					
Calculated	5,730	16.88	0.963	0.046	—
Experimental	5,724	16.91 ± 0.08	0.972 ± 0.006	0.054 ± 0.001	1.69 ± 0.24
<u>Assembly No. 5</u>					
Calculated	22,900	9.40	—	—	—
Experimental	22,900	9.3	—	—	4.425 ± 0.074

to revision of either the value or the assigned error, where quoted. For continuity, data for all assemblies are quoted rather than limiting the information to that obtained during the year. The calculated values are those reported in an internal memorandum by P. Michael from the Reactor Physics Theoretical Group and obtained by the GAM and THERMOS codes. J. PHELPS, E. WEINSTOCK

Van de Graaff

During the report period four sets of experiments were performed using the pulsed neutron source technique: determination of the diffusion constant of polyethylene and the diffusion coefficient anisotropy effect in composite stacks of aluminum and polyethylene; determination of diffusion parameters of light water and an investigation of control rod configurations in water assemblies; investigation of control rod configurations in graphite and comparison of results with one-group theory; and measurement of the prompt neutron decay constant of a well subcritical multiplying system, with and without large water reflectors, and comparison of results with existing few group theory.

The Van de Graaff accelerator produces pulses of deuterons in the range 10- μ sec to 2-msec dura-

tion, with a duty cycle approaching 15%, by means of electrostatic extraction of ions from the rf ionizing source. The deuterons are accelerated to an energy of 1 MeV and produce neutrons through the $\text{De}^n(d,n)\text{B}^{10}$ reaction. These neutron pulses are injected into an assembly to be investigated. At some time after the pulse, neutron thermalization is complete and an equilibrium neutron energy distribution is established in the assembly. The space and energy dependences of the neutron flux are then separable, and the exponential decay in time of the equilibrium neutron population is observed by means of a sequential scaler system. The decay constant can be determined by means of least squares curve fitting of count rate *vs* time. This fundamental decay constant may be simply related to the geometrical buckling of the assembly and the diffusion properties of the medium.

Diffusion Coefficient Anisotropy in Aluminum/Polyethylene Stacks

When a moderating medium is pulsed as described above, the fundamental decay constant, λ , can be written as

$$\lambda = (\Sigma_a v) + D_0 B^2 - C B^4, \quad (1)$$

where $(\Sigma_a v)$ indicates an average value over the spectrum of velocities v , D_o is the diffusion constant, C the diffusion cooling coefficient, and B^2 the geometrical buckling of the assembly. Equation (1) is simply an expression of neutron balance in the system, where $(\Sigma_a v)$ expresses absorption, $D_o B^2$ leakage from system, and CB^4 the cooling effect.

Homogeneous polyethylene stacks with a buckling range 0.034 to 0.310 cm^{-2} were investigated, and preliminary least squares analysis of λ vs B^2 indicated a diffusion constant (corrected for equal hydrogen content of polyethylene and water) smaller than that of water, as predicted theoretically. In this analysis, it was assumed that the contribution of the CB^4 term in Eq. (1) was $<1\%$ of λ , and only a linear dependence of λ upon B^2 was assumed.

Composite stacks of Al and polyethylene in the same buckling range were investigated next. These

stacks were constructed from slabs of $\frac{1}{4}$ or $\frac{1}{2}$ -in.-thick Al and polyethylene to achieve volume ratios of Al:polyethylene of 1:1 and 2:1. Figure 1 illustrates a typical stack. The neutron balance in such stacks is influenced by the streaming of neutrons along the Al channels, since Al with a large mean free path ($\lambda_{tr} = 11.9$ cm) can be considered as void with respect to water ($\lambda_{tr} = 0.5$ cm). Leakage effects can therefore be interpreted in terms of two diffusion constants, $D_{\parallel}$ (parallel to the Al channels) and $D_{\perp}$ (perpendicular to them). Equation (1) can then be written

$$\lambda = [(\Sigma_a v) + D_{\perp}(B_x^2 + B_y^2)] + D_{\parallel} B_z^2 \quad (2a)$$

or

$$\lambda = [(\Sigma_a v) + D_{\parallel} B_z^2] + D_{\perp}(B_x^2 + B_y^2), \quad (2b)$$

where the z -direction is assumed parallel to the aluminum channels and the cooling term is again neglected. If the z -dimension of the assembly is held constant while the x and y dimensions are

Figure 1. Typical aluminum/polyethylene stack (volume ratio 1:1).

changed, Eq. (2b) applies; similarly, if x and y dimensions are constant with changing z -dimension, Eq. (2a) applies.

By means of curve fitting $D_{\perp}$ and $D_{\parallel}$ can then be determined. Initial results indicate $D_{\parallel}/D_{\perp}$ ratios which differ considerably from theoretical predictions (B.C. QUIQUEMELLE, BNL Internal Memorandum, RP 295, January 1965). Re-analysis of the decay data, allowing for the presence of higher spatial modes of the neutron distribution in addition to the fundamental mode, is indicated.

The above experiments were performed by S. Santiago (at present with the Junta de Energía Nuclear, Madrid).

Determination of Diffusion Parameters of Light Water and Investigation of Control Rod Configurations in Water

Cylindrical geometries were used in these experiments. In order to determine the diffusion parameters of water, thin-walled Lucite cylinders of various radii were used as containers, filled with water to various heights, to cover a B^2 range of 0.03 to 0.17 cm^{-2} . Initial values are $(\Sigma_a v) = 4819 \text{ s}^{-1}$, $D_0 = 35,500 \text{ cm}^2\text{-s}^{-1}$.

Control rods were simulated by compressing powdered boron in thin-walled Lucite tubes. Six different rod sizes were examined, with diameters of 0.4 to 2.0 cm. A rod was located along the axis of a cylindrical container, and the fundamental λ of the perturbed system determined as usual. The change in λ from the unperturbed value can then be related to a change in the buckling of the system.

Control Rod Configurations in Graphite

The fundamental decay constant of a graphite assembly was measured. The assembly was then perturbed by the introduction of one or more cadmium rods, the new decay constant determined, and the change in λ compared with the value predicted by one-group control rod theory.

A stack with dimensions $28 \times 28 \times 32$ in. ($B^2 = 0.00496 \text{ cm}^{-2}$) was assembled with GBF graphite bars $4 \times 4 \times 16$ in. and of average density 1.68 g/cc. The entire assembly was contained in a rigid container of $\frac{1}{4}$ -in. Al sheets, lined with 0.033-in. Cd sheets. After any change in rod configurations, the stack could be compressed to exactly the same size as before. The detectors used were two large enriched BF_3 proportional counters external to the stack, wrapped in cadmium except for a window through which they saw similar slits in the cadmium cover around the stack.

Since λ of the homogeneous stack serves as a basis of comparison for every perturbed assembly, particular care was taken in the determination of it.

A value of $998.6 \pm 1.3 \text{ sec}^{-1}$ was obtained, in excellent agreement with a computed value of $997.2 \pm 9.0 \text{ sec}^{-1}$ by using GBF graphite diffusion parameters (E. STARR AND G.A. PRICE, in *Proc. Brookhaven Conf. Neutron Thermalization*, BNL 719 (C-32), Vol. III, p. 1034, 1962). These parameters were adjusted to a graphite density of 1.68 g/cc, and all measured decay constants were normalized to a temperature of 22°C. A decay of 2.57 msec was introduced between the start of neutron pulse and the activation of the first analysis channel of the time analyzer, to allow for thermalization of the neutrons. Due attention was given to the elimination of higher spatial harmonics present in the decay data.

Cadmium sleeves with diameters of 1.28, 1.92, 2.55, 3.82, and 5.15 cm and 32-in. long were rolled from 0.033-in. sheets. These tubes were fully inserted into the stack, fitting snugly into holes that were drilled through graphite bars. These bars were then moved across the stack. Seventy-nine different rod configurations were studied, including rods axially located, single eccentric rods, rings of two or four symmetrically spaced rods, and combinations of an axial rod with one or two eccentric rods. The fundamental decay constant was determined for each case.

Results were compared with one-group theory which considers the absorbing rod as a singularity in the neutron field (G.V. SINYUTIN AND V.N. SEMENOV, *Proc. 2nd IIN Intern. Conf. Peaceful Uses of Atomic Energy*, Vol. 11, p. 253, 1958). This theory is valid only for cylindrical symmetry. The graphite parallelepiped was therefore considered as an equivalent cylinder with the same height, but an effective radius computed by equating the transverse bucklings in cartesian and cylindrical coordinates.

As a first approximation, it may be assumed that the presence of a rod does not alter the diffusion properties of the moderator to a large degree. From Eq. (1) the following expression may then be derived for $\Delta\lambda$, the change in λ due to the perturbation,

$$\Delta\lambda = \Delta B^2 [D_0 - C(2B^2 + \Delta B^2)], \quad (3)$$

where ΔB^2 is the effective increase in buckling of the system. For a given $\Delta\lambda$, Eq. (3) can be solved

numerically for ΔB^2 and this number compared with theoretical prediction. Preliminary results indicate good agreement for the three smallest rods, but for rod diameters in excess of λ_{tr} for graphite (≈ 2.5 cm) agreement is poor. This is illustrated in Figure 2, where percent change in B^2 is plotted vs rod size.

It seems likely that allowance must be made for a neutron spectrum change caused by the presence of a rod. This possibility is to be investigated.

Decay Measurements on a Well Subcritical Multiplying System

The experimental work on the reflected and unreflected uranium metal (1.3% U^{235}) fueled, light water moderated slab lattice has been started. The purpose of the experiment is to investigate whether the pulsed neutron method may be applied to infer the reactivity of a well shutdown reactor ($k_{eff} \approx 0.8$ to 0.5) when this reactor is surrounded by a large and effective reflector.

Figure 2. Percent change in buckling vs axial rod size.

The lattice chosen is one which has already been studied in a series of exponential experiments at Brookhaven [H. WINDSOR, *Trans. Am. Nucl. Soc.* 6, 52 (1963)]. The system is unreflected in two dimensions and a reflector may be added in the third dimension. The method of loading allows the size to be changed easily, yet leaves clean boundaries with no dry fuel protruding so that the geometric buckling may be precisely defined. Reactivity will be changed by two methods: (1) by reducing the height of the system, and (2) by poisoning the moderator in the fueled region only by boric acid. Theory shows that in both cases the pulsed behavior approaches that of the moderator alone as k_{eff} decreases.

The first experiment is $\frac{3}{4}$ complete, and preliminary results are in qualitative agreement with theory. Large and persistent higher decay modes are present, and at low k_{eff} these lie close in decay constant to the fundamental, making the measurement of these cases difficult. It is hoped that these can be corrected for, if not eliminated, without introducing too much uncertainty.

J. MOHR,
G. WELLS

$U^{233}O_2$ - ThO_2 Lattice Experiments

A series of exponential experiments on Zircaloy-clad $U^{233}O_2$ - ThO_2 fueled elements moderated with water and water solutions of H_3BO_3 was completed. Preliminary analysis of the results was carried out and preparations for two series of heavy water moderated exponential experiments utilizing the same fuel were begun.

The experiments were carried out using the $U^{233}O_2$ - ThO_2 fuel produced at ORNL by vibratory compaction of $U^{233}O_2$ - ThO_2 particles. The mixed oxide was prepared by the sol-gel process. The oxide was compacted into $\frac{1}{2}$ -in.-o.d. Zircaloy tubes with 0.035-in. wall thickness and 42-in. active length. The fuel was compacted to a density of 8.96 g/cm³.

This fuel also contained 24 ppm of U^{232} , which was produced as an unwanted by-product during the U^{233} production. The U^{232} decay scheme has several hard γ rays in it. The γ -ray activity grows in and does not reach a maximum until about 10 years after initial chemical separation of the uranium. Their presence necessitated carrying out all major fuel handling semiremotelly. Techniques were developed and continually modified to hold personnel exposure within acceptable limits. All fuel storage and major loadings were done in 11 ft of water. Transfer from the storage area to the ex-

Figure 3. Water shielded fuel storage and loading tank with lattice in loading position.

perimental area was carried out with a remotely operated crane. Direct contact with the fuel was minimized and suitable shielding was arranged when necessary. Figure 3 shows the top of the storage tank with a lattice in position for loading.

Bucklings, reflector savings, and a series of relaxation lengths as a function of core radius were measured for two poison concentrations for each of the moderator to fuel volume ratios 1:1, 1.38:1, 1.71:1, 2.19:1, 3.0:1, and 4.27:1. Only a single poison concentration was measured for the 6.8:1 volume ratio since its clean water buckling was quite low. No poison measurements were performed on the 9:1 volume ratio lattice since its clean water buckling was less than zero. Poison concentrations were chosen so that, in the case of the more concentrated solutions of H_3BO_3 , the measured material bucklings were approximately zero. The intermediate poisons were chosen to reduce the poisoned bucklings to half their clean value.

In each lattice of a given poison concentration and volume ratio, two flux traverses were measured in each of six, 30° apart, radial directions located in the same plane. Four axial traverses were also performed at the top loading. The radial traverses were measured by attaching a foil to

either side of each fuel element on the radii of interest. The resultant corrected activities were fit to a simple J_0 Bessel function by least squares. The reflector transient effects were accounted for by dropping the exterior points from the fit until the fitted value of the extrapolated radius was constant as further points were dropped. This extrapolated radius was combined with the axial relaxation length, measured at the same core size, to give the "flux shape material buckling." The "flux shape reflector savings" was determined as the difference between the actual core boundary and the point at which the J_0 fit radial flux was extrapolated to zero.

In conjunction with measurements of the flux shape material bucklings, a series of relaxation lengths was measured up to 20 core sizes; the core sizes were obtained by adding or removing fuel to the exterior of the core while maintaining its cylindrical geometry. These relaxation lengths and core radii were used as a second method to determine the material buckling (B_m^2) and reflector savings (λ); the series can also be compared directly with theoretical calculations to give a sensitive test of the theory.

Preliminary determination of B_m^2 from a series of relaxation lengths measured as a function of core radius was carried out utilizing the standard formula

$$B_m^2 = (2.405)^2 / (r + \lambda)^2 - (1/L^2), \quad (4)$$

where r is the core radius, L is the measured relaxation length, and λ is considered as (a) a constant [H. J. C. KOUTS, et al., in *Proc. 1st Intern. Conf. Peaceful Uses of Atomic Energy, Geneva*, Vol. V, p. 600, 1956], (b) $\lambda_0 + CB_z^2$ (R. L. HELLENS AND E. ANDERSON, Informal Report BNL 7293), or (c) $\lambda_0 / (1 + CB_{zr}^2)^{1/2}$ [H. H. WINDSOR, *Trans. Am. Nucl. Soc.* 8, 265 (1965)]. λ_0 and C are arbitrary constants but can be interpreted as being related to some physical quantities; B_z^2 is $-1/L^2$ and B_{zr}^2 is $-1/L_r^2$, where r denotes measured in the reflector. Models (b) and (c) both predict that the reflector savings is not constant with core size; it is larger at shorter relaxation lengths (smaller cores). When the data were analyzed using λ as a constant, discrepancies of 4 to 5% existed between those inferred from the relaxation length series and the large core flux shape material bucklings. By introducing model (b) or (c) for the reflector savings into the analysis of the relaxation length series the discrepancies were reduced to 1% or less in the

cases that were compared. Theoretical calculations indicated that λ does increase as the core size is decreased; direct flux shape measurements of the same core at two different sizes (hence different B_z^2 or B_{zr}^2) did give larger values of λ for the smaller cores.

Preliminary analysis of the clean water lattice in which the flux shape reflector savings values and behavior were compared with the behavior predicted by theoretical calculations [H.C. HONECK AND B.R. SEHGAL, *Trans. Am. Nucl. Soc.* 7, 214-15 (1964)] and with the values and behavior determined from the series of relaxation length measurements (using model (c) for the reflector savings) indicated that the clean water reflector savings were systematically too large. Model (c) for the reflector savings suggested that this was due to the reflector exhibiting a shorter relaxation length than the core in the region the flux shape measurements were made. This was experimentally checked and found to be the case. All the poison lattice measurements were subsequently carried out higher in the core in a region where the core and

reflector relaxation lengths were equal. The clean water moderated lattice radial flux distributions were repeated higher in the core in the region where core and reflector relaxation lengths were equal. The new reflector savings were from 1 cm in the 9:1 lattice to 0.1 cm in the tight lattices, less than the values measured in the lower region.

Preliminary analysis of the poisoned water lattices indicates that the data are consistent. Table 2 gives preliminary flux shape B_m^{21} s and λ 's for both clean and poisoned lattices.

Preparations were begun for a series of uniformly fueled heavy water moderated exponential experiments and also for a heavy water series using 31 fuel elements clustered in cans of organic coolant. Both these experiments will use the $U^{233}O_2$ - ThO_2 fuel.

Design of the heavy water piping, pumping, and storage tank systems was completed. The main storage tank was installed and a neutron shutter system was constructed that will be used to determine the γ - n contribution of the source reactor to the experiments. The design for the exposure tank,

Table 2
Preliminary $U^{233}O_2$ - ThO_2 Flux Shape Material Bucklings and Reflector Savings

Vol moderator/ vol fuel	Concentration of H_3BO_3 in moderator, mg/ml	Number of fuel elements	Core radius, cm	Relaxation length, cm	Flux shape reflector savings, cm	Flux shape material buckling, M^{-2} , ± 0.7
0.9970	0.0	511	18.90	39.57 ± 0.40	7.11 ± 0.11	79.10
	13.3	889	24.95	21.61 ± 0.03	5.26 ± 0.04	42.04
	25.0	889	24.95	14.88 ± 0.01	5.12 ± 0.10	18.91
1.3840	0.0	397	17.98	43.18 ± 0.30		
	7.8	859	26.41	40.79 ± 0.30	5.44 ± 0.04	50.86
	22.9	889	26.90	13.79 ± 0.03	5.13 ± 0.05	3.72
1.7134	0.0	337	17.54	39.76 ± 0.50	6.50 ± 0.12	93.76
	4.7	625	23.88	40.36 ± 0.28	5.65 ± 0.06	60.16
	18.0	889	28.50	13.81 ± 0.02	5.25 ± 0.05	-1.59
2.1943	0.0	301	17.82	44.5 ± 0.40		
	4.7	661	26.39	42.34 ± 0.13	5.70 ± 0.06	50.47
	13.3	889	30.65	14.82 ± 0.04	5.45 ± 0.03	-1.08
3.0043	0.0	271	18.75	45.18 ± 0.50	6.42 ± 0.16	86.6
	5.0	889	33.98	31.70 ± 0.16	5.69 ± 0.04	26.82
	7.8	889	33.98	16.96 ± 0.03	5.77 ± 0.04	1.85
4.272	0.0	265	21.07	37.97 ± 0.50	6.27 ± 0.05	70.41
	2.7	721	34.80	29.29 ± 0.14	5.88 ± 0.07	23.35
	5.0	721	34.80	15.34 ± 0.04	6.01 ± 0.05	-7.67
6.8449	0.0	433	32.52	39.73 ± 0.50	6.23 ± 0.03	32.17
	1.7	433	32.52	14.38 ± 0.05	6.96 ± 0.14	-11.25
9.2747	0.0	349	33.25	16.32	6.60 ± 0.06	-1.11

grid plates, fuel drier, and special handling tools for carrying out the uniform lattice experiments were completed. Preliminary design of the cluster lattice experiments was carried out.

G. PRICE,
H. WINDSOR

$U^{233}O_2$ - ThO_2 Miniature Lattice Experiments

The miniature lattice assemblies are made up of fuel rods with the same diameter and composition as those in the full-size U^{233} -Th oxide lattice program, but with an active length of 16 in. These short rods are placed in cylindrical lattices with a diameter of 11 in., and with the same range of volume ratios as the full-size lattice program. The number of fuel rods used varies from 61 in the 9.3:1 lattice to 181 in the 1:1 lattice.

The determination of the microscopic parameters of a lattice requires a relatively high neutron flux to activate the foils used in these measurements. The resultant radioactivity of a miniature lattice is not excessive, whereas in the full-size lattice, the activity would seriously impede the handling of the fuel. For this reason, as well as for the greater ease of placing the removed foils in the short fuel rods of a miniature lattice, the microscopic parameters of the U^{233} -Th system are measured in the miniature arrays.

The thermal disadvantage factors of $U^{233}O_2$ - ThO_2 lattice assemblies moderated with light water were measured during the report period. The moderator-to-fuel volume ratios measured ranged from 1:1 to 9.3:1. The differential method was used for the measurement, using small dysprosium-aluminum foils as point detectors.

Measurements of ρ_{02} have begun on the same fuel. The principal technique used is the thermal activation method with intermediate foils of dysprosium and manganese. In this method, the thermal and epicadmium activations of thorium are separated by comparison with the activity of the intermediate foil which has a large cadmium ratio in the lattice. The advantage of this method is the absence of cadmium in the lattice. In some of the lattices, the results from this method will be compared to the results of a direct cadmium ratio measurement.

A new method was investigated for measuring fast fission factors. The method consists of counting the individual fission tracks produced in a piece of plastic that is placed next to the fuel during an irradiation. The principal advantage of this method is the elimination of a double fission chamber calibration.

W. TUNNEY

Beam Experiment Test Assembly (BETA)

Measurements on the Beam Experiment Test Assembly were concluded. This assembly was used to test the effect of fuel element modifications on the quality of external thermal neutron beams in swimming pool research reactors. The fuel elements were modified by eliminating the fuel from the central section of the element. In this manner several different reactors were constructed in which there was no direct line of sight between the detectors used by the experimenter and the fuel in the core. It has been found that wherever the beam tube diameter matched the height of the gap, the unwanted fast neutron and gamma current was decreased by a factor of 6.6 from that for an ungapped core. Similarly, the gamma-to-thermal neutron ratio decreased by a factor of 2.9 from that for the ungapped core. There was a reduction of thermal neutron beam per unit power of 0.33.

A number of experiments were done to check the reactor physics parameters of the split core. Neutron lifetime, control rod calibrations, temperature coefficient, void coefficient, and criticality characteristics were obtained. From the operational point of view, it has been found that the split core is appropriate for reactor powers up to 1 MW but that further measurements would be needed before the concept could be extended to higher powers.

K. DOWNES, A. COURT, C. SASTRE

Neutron Migration Anisotropy

A program to study anisotropic neutron migration has been initiated. To satisfy the need for unambiguous data in this area, a series of clean, direct measurements of directional migration properties will be made in simple systems.

During the year the design and fabrication of the initial experimental equipment were completed, a set of computer codes was written to correct and analyze the experimental data, and the first experiments got under way. The experiments were designed to use the Neutron Source Reactor II, which was also completed during the year.

Currently under investigation is a system of ¼-in.-thick Al plates, spaced ¼ in. apart in water. Both the slowing down distribution from fission to indium resonance energy and the thermal neutron diffusion length perpendicular to the slabs are being measured. The former, along with providing

the first element of the anisotropy study, will yield a value for the neutron age in Al-H₂O.

Although the program is primarily experimental at present, considerable theoretical interest has been shown in this topic at Brookhaven and elsewhere over the past year. Thus calculations are being performed in both the thermal and slowing-down region to compare with the experiments. Preliminary calculations indicate that the anisotropy in the slowing-down region, specifically in the age, is quite small. In the thermal region, large anisotropies (of the order of 2 in the ratio of diffusion lengths parallel and perpendicular to the plates) have been estimated. P. PALMEDO

Cross Sections of Transuranium Elements

Theoretical studies of the production of high *Z* isotopes (Pu²³⁸, Cm²⁴⁴, Cf²⁵², etc.) have indicated that significant advantages might be gained by using epithermal rather than thermal neutron irradiations. Further information concerning nuclear cross sections is needed, however, before a definite conclusion can be reached.

The possibilities of obtaining energy-averaged coarse group cross sections from reactivity measurements on small samples in critical assemblies with different spectra have been investigated. Three assemblies were chosen with median fission energies of 32, 6, and 0.5 keV. Sixteen-group *S*₄ calculations were made for determining the real and adjoint fluxes in the assemblies. Reactivity experiments were then simulated on a number of isotopes with known group cross sections.

From the reactivity response per atom of a sample in the three assemblies, a set of three-group cross sections could be deduced. These cross sections agreed within $\approx 40\%$ with the values obtained from the collapsed 16-group set for all six isotopes studied. However, in a real experiment large corrections have to be made for threshold fissions, etc. With due consideration to the uncertainties in these corrections, it was found that experiments of the proposed type could not yield results accurate enough to justify the necessary effort to perform them.

An investigation has also been made concerning the possibility of improving the knowledge of the thermal cross sections and resonance integrals of the isotopes involved in the production of the above-mentioned materials. The study indicates that one should, in fact, be able to obtain more accurate values than are available at present from a

series of careful reactivity measurements in thermal assemblies. Detailed planning of such experiments is under way, the main problem being the procurement of the highly active samples in suitable form. E. HELLSTRAND

Settled Bed Critical Experiment

A series of experiments was performed to test the feasibility of using a critical experiment to study the packing density of fuel spheres in a settled bed reactor. A conceptual design of such a reactor experiment has been proposed, consisting of enriched U-Al plates in water with a central test region $\approx 6 \times 6 \times 24$ in. which was to be filled with U-Al spheres and water. Changes in the packing density of the test region were to be measured by changes in the excess reactivity of the reactor. The experiments described here were designed to determine the sensitivity of the method, since the available reactor calculations were not particularly accurate for the range of aluminum-water volume ratios to be encountered in a settled bed.

The first critical assembly (runs No. 1 to 3, Table 3) contained 28 fuel elements, each $2.8 \times 3.2 \times 24$ in., and was somewhat irregular in its over-all dimensions. It contained 6.6 kg U²³⁵, 175 kg Al, and had a 39/61 water-to-metal ratio by volume. The assembly was fully reflected by water on all sides. Changes in excess reactivity were observed as U and Al plates were removed from the central fuel element.

The second critical assembly (runs No. 4 to 7, Table 3) contained 7.6 kg U²³⁵ and 213 kg Al. The dimensions were $\approx 17 \times 19 \times 24$ in., and the assembly was fully reflected on all sides by water. It had a water-to-metal volume ratio of 35/65. A test cell, $\approx 5.7 \times 3.2 \times 24$ in. was located midway between the reactor center and outer edge. Changes in excess reactivity were observed as U and Al plates were removed from or added to different regions of the test cell under various conditions (wet or dry).

Runs No. 5 to 7 were performed with no U in the test cell. These conditions simulated a test cell of Al spheres with and without water (wet or dry). Under these conditions the void (nonmetal) coefficient of reactivity was considerably reduced from the case where the test cell contained U. However, it was observed that the coefficient of reactivity reversed sign in various regions of the test cell. Thus, with no U in the test cell it would be practically impossible to correlate over-all void fraction changes with reactivity effects.

Table 3

Reactivity Coefficients in U²³⁵-Al-H₂O Reactor

Run No.	Test cell composition	Change in test cell	Void fraction (nonmetal), %	Change in reactivity, ϕ	Reactivity coefficient
1	474 g U ²³⁵				
	12510 g Al (wet)	Remove 790 g Al		+55.83	+0.0706 ϕ /g Al
2	(wet)	Add 79 g U ²³⁵		+54.59	-0.6909 ϕ /g U
3 ^a	(wet)	Remove 96.35 g Al + 3.65 g U	39.4 to 39.867	- 4.29	-9.19 ϕ /($\Delta\%$ void)
4	474 g U ²³⁵				
	12510 g Al (wet)	Remove 337 g Al + 20 g U	35.4 to 39.3	-13.0	-3.3 ϕ /($\Delta\%$ void)
5	0 g U ²³⁵	Remove 364 g Al	34.7 to 38.4	- 2.6	-0.7 ϕ /($\Delta\%$ void)
	12668 g Al (dry)				
6	0 g U ²³⁵	Remove 364 g Al	33.5 to 37.5	+ 1.3 (edge)	+0.325 ϕ /($\Delta\%$ void)
	12896 g Al (wet)			- 1.2 (center)	-0.300 ϕ /($\Delta\%$ void)
7	0 g U ²³⁵	Add 137 g Al	33.5	+ 0.5	+0.355 ϕ /($\Delta\%$ void)

^aRun No. 3 was not actually performed but was inferred from runs No. 1 and 2.

The results of runs No. 1 to 4 indicate the feasibility of using a critical experiment to measure changes of void fraction in a settled bed. Limitations imposed by probable errors in reactivity measurements lead to uncertainties of about $\pm 0.05\%$ in void fraction as measured by this technique, since individual reactivity measurements have an uncertainty of about $\pm 0.3 \phi$. However, because of the high cost of fabricating U-Al spheres and because of the availability of more precise methods to measure void fractions, it was decided to terminate further investigation along these lines.

G. PRICE, H. WINDSOR

Re-examination of BNL Report WASH 740

Work was completed and a memorandum submitted to the Division of Licensing and Regulation of the Atomic Energy Commission. At the beginning of this project it was expected that a complete review of this field including the large amount of new information would permit a much more definitive report to be written. In actual fact, there are still too many speculative assumptions that must be made. Thus, any new report would not be substantially different from the original. Various new computing techniques developed for this project will be described in technical reports.

K. DOWNES, A. COURT

Neutron Source Reactors I and II

NSR II was taken to the design power of 100 kW for the first time on August 10, 1965. Since

that time the reactor has been used as a source of neutrons for two different sets of experiments: neutron age in aluminum-water mixtures, and microscopic parameter measurements in uranium-thorium oxide lattices. The total integrated power for the report period is slightly more than 4.2 MWh.

Prior to August 1965, a series of critical experiments was performed in order to establish that the reactor could be operated within the operating limit agreement with the AEC. With these requirements fulfilled, the assembly was carried through a series of start-up tests at low power. The system was checked for flow stability under design conditions for 100-kWh operation. The series of start-up tests was concluded with adjustment of the excess reactivity of the assembly, placement of additional shielding around the assembly, and calibration of power using a noise analysis technique.

During the year a set of operating limits for Neutron Source Reactors I and II was generated. These limits were agreed to by the group of Responsible People, the Reactor and Critical Experiment Safety Committee, the Laboratory Director, and the Atomic Energy Commission. Operation of the Neutron Source Reactors under these limits began on February 15, 1965.

The flexibility introduced into the experimental programs as a result of the wide range of powers available in NSR II led to a program of upgrading NSR I, the original source reactor in the Critical Facility. The design power for NSR I was 100 kW.

However, the instrumentation and exterior plumbing system of the reactor were adequate for operation up to a few kilowatts only. A new console system and plumbing system appropriate for 100-kW operation have been constructed and will be installed.

K. DOWNES, A. COURT

HFBR Start-up

The Reactor Physics Experimental Group is assisting the Reactor Operations Division in the start-up of the High Flux Beam Reactor (HFBR). The necessary equipment to monitor the initial loading of the HFBR, and to measure the physics parameters of the reactor after loading, has been built and moved to the reactor building. This equipment includes the Experimental Group analog computer that has been placed in the HFBR control room for use in the start-up experiments. An operating manual (C. SASTRE, *HFBR Physics Start-up Manual*, Informal Report BNL 9591) for the start-up experiments was prepared and was submitted to the AEC for approval at the end of October 1965. The manual has been reviewed and approved by the BNL Reactor and Critical Experiment Safety Committee.

The start-up experiments which the Experimental Group will carry out on the HFBR are: (a) Initial reactor loading and criticality. (b) Final determination of the effectiveness of the photoneutron delayed groups in the HFBR. (c) Control rod calibrations, shadowing effects of the rods, and determination of the total cold, clean reactivity of the fully loaded core. (d) Helium pressurization and bubble effects on reactivity. (e) Coolant flow effects on reactivity. (f) Neutron lifetime measurement. (g) Uniform temperature coefficient of reactivity measurement. (h) Reactivity worths of the irradiation thimbles and of standard samples in the thimbles. (i) Reactivity measurements on partially loaded cores. (j) Reactor noise measurements. (k) Power coefficient of reactivity measurements. (l) Xe reactivity effects at various power levels. (m) Neutron beam current measurements in various beam holes. (n) Equipment vibration surveys and measurements.

A substantial effort has been necessary during the current report period to prepare for the start-up experiments. The experiments themselves will begin with the initial loading of the HFBR and will take 4 to 6 months to complete.

C. SASTRE,
K. DOWNES, A. COURT, E. WEINSTOCK,
W. TUNNEY, A. SABASTO, J. HENDRIE

ADVANCED TESTING AND RESEARCH REACTOR GROUP

J. HENDRIE

Pulsed Fast Research Reactor Studies

A review of various possible advances in research reactor capabilities has led to the concept of a pulsed fast reactor. The needs of the experiments in solid state and nuclear physics are always in the direction of more intense beams at relatively low energies, with an accompanying reduction in fast neutron background. These are precisely the criteria which led to the design of the High Flux Beam Reactor, and it is already clear that the next step in research reactors beyond the HFBR will have the same requirements. It is believed that a substantial (i.e., by a factor of 30 to 100) increase in neutron beam current over that available from the HFBR is not in sight from a constant-power fission reactor in view of the present and near-future state of the art.

One line of attack on the problem is to build high energy, high current accelerators, and use the neutron spallation from protons on heavy nuclei as a source. Groups in Canada and at Oak Ridge are currently following this line. It is believed that the accelerator-spallation reaction source is a promising system but one which will involve a very large and expensive development program and an even larger construction effort.

A second line of attack, which might lead to a useful research reactor at a more moderate cost and much earlier, is the pulsed fast reactor. In this approach a small fast reactor is repetitively pulsed by periodic reactivity surges into the super-prompt critical region. The repetition rate would fall in the range 10 to 100 pulses/sec. Experiments to be done at a pulsed reactor facility would all use some form of the time-of-flight technique for energy measurement. Time-of-flight methods are now used at many research reactors, with the pulsed neutron beams being formed by mechanically chopping the steady beams. A pulsed reactor is obviously an advantage for such experiments. It also appears that many experiments which are now done with steady beams could be converted to the time-of-flight method.

There is one pulsed fast reactor now in operation. This is the Russian IBR machine at Dubna. It has an average power of 3 kW, with a peak power in the pulse of about 20 MW. The IBR is gas-cooled, has Pu^{239} and U^{235} for fuel, and is op-

erated with two wheels to give the reactivity pulses. The repetition rate may be varied from 4 to ≈ 50 pulses/sec. A second pulsed fast reactor has now reached the stage of a complete conceptual design, with a decision on construction to be made in the near future. This is the SORA machine, designed by a group at the Ispra laboratory of Euratom. The SORA design has U^{235} fuel, is sodium cooled, and will operate at 0.5 to 1-MW average power. It is a single wheel design, with a reflector block of Be passing by the core to give the reactivity pulses. The repetition rate is fixed at 50 pulses/sec. The peak power in a pulse is ≈ 300 MW.

The SORA group has considered the effectiveness of the pulsed reactor, as compared to a constant-power reactor, in providing neutrons for experiments. They conclude that the 1-MW SORA machine is equivalent (in terms of counting rates in the experiments) to a 280-MW constant-power reactor for cold and thermal neutrons, and to a 420-MW constant-power reactor for epithermal neutrons. The pulsed reactor does have the disadvantage of larger pulse widths than one might like for time-of-flight analysis (90 μ sec for thermal and 50 μ sec for epithermal neutrons). The SORA

people find that operating a synchronous chopper with the pulsed reactor to give widths of 20 and 5 μ sec for thermal and epithermal neutrons, respectively, would reduce the 1-MW pulsed machine to something equivalent to 70 and 50-MW constant-power reactors, for thermal and epithermal neutron experiments. The advantage of the pulsed system as a neutron source is still large, even with the choppers.

In the pulsed fast reactor studies at BNL, the possibility is being examined of increasing the average power of the system to 15 to 20 MW, and using a two-wheel design to give some variability in the repetition rate. At lower repetition rates the peak power in the pulse may be increased for the same average power. Some experiments would benefit by having larger power pulses at a slower repetition rate, while others might require a rapid repetition rate at lower peak power. Such a system, on the basis of the SORA comparisons, would be equivalent to a constant-power reactor of the HFBR type at powers of 2000 to 10,000 MW, and would thus provide the substantial increase in source intensity that is believed necessary for the next step forward in research reactors.

The pulsed fast reactor studies during the report period have included criticality and prompt neutron lifetime calculations, calculations of the kinetics of pulsed operation and of pulse shapes, a survey of potential fuel materials and forms, and some preliminary experiments on coolant flow characteristics and pressure drop in one type of core.

In the survey of fuel materials, particular attention has been paid to Pu and PuO_2 . The small delayed fraction in Pu^{239} fission gives a larger reactivity swing in the pulsed mode, for a given motion of fuel or reflector, than does that in U^{235} . The essential properties of the fuel material are the tensile strength at operating temperature and under radiation conditions, and the thermal conductivity. The pulsed mode of operation imposes a high frequency thermal cycle on the fuel, and the ability of the fuel to withstand the resulting stresses and to deliver the heat generated to the coolant determine the allowable peak power.

Five cermet fuel materials are under consideration: PuO_2 in stainless steel, PuO_2 in Fe, PuO_2 in Al, PuO_2 in sintered Al powder (SAP), and $PuAl_3$ in Al. Unfortunately, little or no data exists for several of these materials, particularly under radiation conditions. By using the existing data (with various extrapolations), it has been possible to construct a graph of "performance factor," the prod-

Figure 4. Performance factor of various plutonium fuels for pulsed reactor.

uct of tensile strength and thermal conductivity, as a function of PuO_2 volume fraction for the first four materials listed. This graph is shown in Figure 4. As is not uncommon in preliminary reactor design work, the fuel material which appears best from this figure is the one with which there is the least experience, in this case PuO_2 -SAP.

The criticality calculations have thus far been limited to homogeneous spherical reactors of Pu or PuO_2 , Fe, and Na, with reflectors of Fe. The calculations have been done with multigroup diffusion codes and by the S_4 transport method. The first series set core volume at 5 and 10 liters, sodium volume fraction at 0.30, and asked what Pu loading was necessary to give a $k_{\text{eff}} = 1.1$. The 5-liter core required 27 kg of Pu, and had a prompt lifetime of 5×10^{-8} sec. The 10-liter core required 37 kg of Pu, and had a lifetime of 6.5×10^{-8} sec. The second series of calculations represented PuO_2 cermet fuels in plates and packed spheres. The core compositions were chosen from the standpoint of fueled plates or spheres with reasonable clad-

ding thickness and cermet proportions to give fuel elements which could be easily fabricated with existing techniques, and which should stand the pulsed reactor thermal loads and radiation levels. Table 4 gives the input parameters and the results of the calculations. The effect of various reflector materials was examined in a third series of calculations; Table 5 gives the results.

A series of survey calculations has been made on the kinetics of the pulsed operation of the reactor. The calculations have been limited to reactors fueled with Pu, with a delayed neutron fraction of 0.002. Since the repetition rates being considered are all large compared to the decay periods of the delayed neutron precursors, the fluctuations in the delayed neutron source are small (compared with the mean value of the delayed source) and can be ignored.

The power pulse of the reactor is determined by the reactivity pulse, and the latter has been assumed to result from the rotation of a reflector block or a fissioning block past a stationary core. There is a practical relation between the pulse repetition rate and the duration of the reactivity pulse due to these assumptions about the geometry of the system. For instance, in single wheel machines, a rotor moves the reflector or fission block past the core once each revolution. The portion of each revolution during which there is a reactivity effect from the moving block links the reactivity pulse duration to the repetition rate. To describe this relation, we define a "form factor" as the *inverse* of the angular fraction over which the reactivity of the system is changing. Form factors of 20 to 40 were considered in the survey calculations, these being around the expected value of 30 for a

Table 4

Pulsed Reactor Preliminary Criticality Calculations

Core type	Plates	Packed spheres
Input		
Geometry for calculation	Spherical	Spherical
Volume fractions		
Na	0.39	0.30
Fe	0.45	0.28
PuO_2	0.16	0.42
Density, g/cc		
Na	0.832	0.832
Fe	7.86	7.86
PuO_2	11.46	11.46
Reflector thickness, cm	61	61
Required k_{eff}	1.1	1.1
Results		
Core radius, R , cm	22.1	15.2
Core volume, liters	45.1	14.8
Mass Pu^{239} , kg	73.1	41.8
Prompt neutron lifetime, sec	3.4×10^{-7}	2.3×10^{-7}
Median flux energy, MeV	0.39	0.51
$(\Delta k/k)/(\Delta R/R)$	0.975	0.979
Core size at critical, from reactivity coefficient		
Radius, cm	20.6	14.12
Volume, liters	36.6	11.8
Pu^{239} mass, kg	59.3	33.3
Sodium temperature coefficient, $(1/k)(\Delta k/\Delta T)$, $^{\circ}\text{C}^{-10}$	6.0×10^{-6}	4.1×10^{-6}

Table 5

Pulsed Reactor Preliminary Reflector Calculations

Core type	Plates, k_{eff}	Packed spheres, k_{eff}
Configuration		
Core/61 cm Fe	1.10	1.10
Core/2 cm Be/61 cm Fe	1.189	1.189
Core/5 cm Be/61 cm Fe	1.300	1.304
Core/5 cm Li^7 /61 cm Fe	1.04	1.016
Core/5 cm Li^6 /61 cm Fe	0.735	0.763
Core/5 cm Li^6 /5 cm Li^7 /61 cm Fe	0.761	0.768
Core/5 cm Li^7 /5 cm Li^6 /61 cm Fe	0.765	0.767
Bare core	0.612	0.600

Figure 5. Power and pulse width *vs* repetition rate. Prompt subcriticality = -0.03 ; lifetime = 2×10^{-8} sec; delayed fraction = 0.002 .

20-cm interaction distance and a 200-cm-diam wheel.

The condition that succeeding power pulses should be of the same size in the pulsed mode gives a direct relation between the magnitude of the reactivity pulse and repetition rate. In the survey calculations three values of minimum prompt reactivity or "prompt subcriticality" (i.e., the reactivity base line between pulses) were chosen. For each such value, a series of repetition rates was chosen, and the corresponding maximum prompt reactivities were determined. The calculation then assumes a parabolic reactivity pulse between these minimum and maximum values, with a duration given by the form factor. The power pulse shape is calculated together with various power and energy ratios. The results of these calculations are shown in Figures 5, 6, and 7. The "prompt subcriticality" of -0.03 in Figure 5 corresponds to the reactivity swing available from pulsing with a reflector block alone. The cases shown in Figures 6 and 7, with minimum prompt reactivities of -0.06 and -0.10 , respectively, would require moving a block of fissionable material, probably in conjunction with a reflector block. A typical power pulse is shown in Figure 8. The effects of varying the prompt neutron lifetime are shown in Figure 9. The maximum prompt reactivity necessary for steady pulsing increases as the lifetime lengthens, as does the pulse width.

Figure 6. Power and pulse width *vs* repetition rate. Prompt subcriticality = -0.06 ; lifetime = 2×10^{-8} sec; delayed fraction = 0.002 .

Core design studies have been made on two types of cores. The first of these is a plate-element core having a sodium fraction of 0.39 . The fuel is a cermet of 40 vol % PuO_2 in stainless steel.

The cermet is clad with steel in plates of 0.100 in. total thickness and 0.010 in. cladding thickness. The fuel width is 2.000 in., and the total plate span is 2.120 in. The plate length is 14 in. A total of 480 such plates are held in an array 13.5×13.9 in. in cross section. The sodium coolant channels between plates are 0.073 in. thick. The plate core would have a coolant temperature rise of $\approx 75^\circ\text{F}$ at a flow rate of 7000 gpm. The sodium velocity in the core under these conditions is 30 ft/sec, and the core pressure drop should be in the range of 10 to 15 psi. The fuel cermet temperature rise during a pulse is 27°F , average, for a 1-MW-sec pulse energy, and proportionately less for smaller pulses.

The second core design is based on the ordered arrays of fuel spheres which have been developed in the settled bed reactor program at BNL. In these cores, fuel spheres are stacked in a container in a square-base, rhombohedral pattern, with horizontal ball spacings 7 to 20% larger than the ball diameter. This type of core should be able to sustain a much larger thermal shock than the plate core, because of the small dimensions of the individual fuel elements (about $\frac{1}{4}$ in.), and the ability of the whole bed to accommodate thermal expansion without lateral forces on the container. A

Figure 7. Power and pulse width *vs* repetition rate. Prompt subcriticality = -0.10 ; lifetime = 2×10^{-8} sec; delayed fraction = 0.002 .

principal difficulty in the design of such a core has been the uncertainty as to the coolant pressure drop in the bed. The literature contains data on pressure drop in tight-packed, ordered arrays of spheres, where the ball spacing is just equal to the ball diameter [J. J. MARTIN, W. L. McCABE, AND C. C. MONRAD, *Chem. Eng. Progr.* **47**, 91 (1951)]. There are methods for correcting the bed pressure drop for increased void volume which have been tested in randomly packed beds, but it was not clear that these methods would be correct for the loose-packed ordered bed. The loose-packed ordered arrays have never been studied experimentally.

A brief experiment on pressure drop has been carried out in arrays of $\frac{1}{4}$ -in.-diam spheres, with water as the fluid. Reynolds numbers from 1000 to 15,000 were covered in the experiment, with three different ball spacings, and with several bed depths. The Reynolds number is defined for these systems as the ratio $D_p \rho_f V_o / \mu_f$, where D_p is the ball diameter, ρ_f and μ_f are the fluid density and viscosity, respectively, and V_o is the "superficial" fluid velocity in the bed (i.e., the velocity which would exist in the container if the spheres were removed). The results of the experiment are shown in Figure 10, where the friction factor is plotted against Reynolds number. The friction factor is defined as the ratio $\Delta P g D_p / 2 L \rho_f V_o^2$, where ΔP is the pressure drop, g the gravitational acceleration, L the bed

Figure 8. Power pulse shape. Prompt subcriticality = -0.1 ; repetition rate = 50 pps; form factor = 30; lifetime = 2×10^{-8} sec; delayed fraction = 0.002 .

Figure 9. Pulse width and maximum prompt reactivity *vs* lifetime. Prompt subcriticality = -0.06 ; repetition rate = 40 pps; delayed fraction = 0.002 .

Figure 10. Friction factor *vs* Reynolds number for square-base, rhombohedral arrays of spheres.

depth, and the other terms are defined above. The three ball spacings were at 1.071, 1.148, and 1.200 times the ball diameter. The fluid volume fractions (ϵ) at these spacings are 0.300, 0.318, and 0.313, respectively. The data of Martin et al. are shown in Figure 10 for comparison. A correction for fluid void fraction has been made in the Martin data to match the void fractions in the experiment. It is clear that the standard void correction is not applicable to the ordered bed arrays, and that the void channels which appear in the ordered bed substantially reduce the pressure drop. An extension of these preliminary experiments is under way to obtain final values for friction factors, and to resolve questions of the end corrections, side-wall effects, and the dependence of the friction factor on ball size.

On the basis of the friction factors determined in the experiment, a preliminary design for an ordered bed core has been made. The ball size is 0.25 in. diam, with a spacing of 1.17 ball diameters in the horizontal direction. The core is square in cross section, 12.4×12.4 in., with a depth of 6.8 in. The sodium flow rate is 2500 gpm, giving a pressure drop of 120 psi and a temperature difference of 204°F at 20-MW average power. The average power density is 1.18 MW/liter. The average temperature rise in the fuel spheres for a 1-MW pulse is $\approx 38^\circ\text{F}$. J. HENDRIE, C. SASTRE, J. FELBERBAUM, M. LEVINE, A. ARONSON, G. PANCER, T. SHEEHAN

HFBR Dynamics

In expectation of the start-up of the HFBR in 1965, a detailed re-analysis of stability and accident dynamics was undertaken. This analysis covered both space dependent and space independent aspects of the problem. Six internal memoranda were issued as follows.

1. An analysis of the HFBR Temperature Dynamics, April 21, 1965.
2. On the Separation of Core and Reflector Reactivity Coefficients in the HFBR, May 6, 1965.
3. Prompt Critical Transients in the HFBR, June 7, 1965.
4. Xenon Dynamics of the HFBR, July 14, 1965.
5. Temperature Dynamics of the HFBR, July 14, 1965.
6. The HFBR Transfer Function and Oscillator Calculations, August 20, 1965.

G. LELLOUCHE, J. CHERNICK

Direct Conversion

J. POWELL

NONEQUILIBRIUM PLASMAS - DIRECT IONIZATION BY FISSION FRAGMENTS

The work on the conductivity of a gas bombarded by fission fragments has continued toward the ultimate aim of understanding the mechanism governing this phenomenon and determining whether it can be suitable for a plasma MHD device. Such a device would have the advantage over all previous plasma MHD concepts in that the ionization in the MHD generator could be made independent of current density, eliminating the problems of breakdown and short circuits that have prevented the development of practical non-equilibrium MHD generators.

Experimental Studies

Work has centered on improving apparatus and methods in preparation for a more definite series of experiments, and in analyzing the data. Some of the salient facts revealed are that: the effective electron temperature at equilibrium, when fission fragments are bombarding the (Ne + 0.1% Ar) mixture, is of the order of 2500°K , as measured with Johnson-Malter double probes (see Figures 11 and 12 for typical results). The effective recombination process reaction rate can be favorably influenced (decreased) by increasing the electric field to values such as would be generated typically in a plasma MHD duct. This latter is to be expected in a situation where the ionization is not uniform, but highly concentrated at randomly distributed locations throughout the plasma, as is the case here

Figure 11. Double probe current vs potential.

Figure 12. Double probe temperature determination plot.

where the ion-electron pairs tend initially to be localized along the fission track.

Theoretical Studies

As regards this latter point, a theoretical study is being made with the aid of a digital computer of the changes with time in the density of ions, electrons, and neutrals, and their velocity distributions, in the column of ionization produced when the fission fragment traverses a gas. The initial distributions in phase space are assumed as might be calculated, for example, classically, using the impulse approximation to ionization by a swift charged particle passing through matter, and the subsequent evolution of the various distributions is followed as time incremented. The influence of electric fields and collisions and recombinations of various sorts are to be taken into account. It is hoped that experimentally observed quantities such as the electron temperature can be obtained, and a description of the column of ionization as it changes with time will result.

EXTENDED LIFETIME PLASMAS - INDIRECT IONIZATION BY METASTABLE MOLECULAR STATES EXCITED BY FISSION FRAGMENTS

It may be possible to extend the lifetime of plasmas beyond the submillisecond ion-electron recombination time by using long-lived energy carriers to reionize the gas. These carriers could be free radicals or metastable electronic/vibrational states produced by fission fragment bombardment. The main advantage of extended lifetime plasmas over the method discussed above is that excitation can be produced by fission fragments in the reactor upstream of the MHD generator. If the generator and

Figure 13. Long-lived afterglow plasma in nitrous oxide.

reactor are separated, severe constructional and electrical problems are eliminated. Work has concentrated on two areas to date: experiments to investigate the properties of plasmas with lifetimes of ≈ 1 sec (produced by rf discharges), and whether such plasmas could be useful in MHD generators.

RF Plasmas

At very high frequencies, e.g., 100 Mc, and high power input, e.g., 20 kW, a point discharge produces a plasma ball which will persist up to 1 sec after the input power is cut off. Figure 13 shows a photograph of such a ball. They are typically 4 in. in diam and range in color from yellowish to white. They radiate light at ≈ 50 -W power. These balls can be produced in oxygen, nitrogen, and mixtures and compounds thereof, but not in the noble gases.

This is the first time, to our knowledge, that such long-lived plasmas have been produced in the laboratory. They may exist in nature as "ball lightning" where lifetimes of several seconds are reported.

The lifetime is a factor of several hundred longer than the lifetime for thermal radiation from a hot gas, or for electron-ion recombination. The required density of energy carriers is too great for recombination of free radicals, i.e., $N + N \rightarrow N_2$. The recombination rate at this density would be many

orders of magnitude too large. Since the balls are produced in pure oxygen and nitrogen, it cannot be combustion.

There are only two possibilities – metastable electronic or vibrational states. The former can store 4 to 5 eV/molecule while the latter can store 1 to 2 eV. However, vibrational lifetimes of >0.1 sec are not possible in O_2 and are possible in N_2 only if the translational temperature is well below $600^\circ K$. However, these long-lived plasmas can be produced in O_2 and N_2 well above $600^\circ K$, with no appreciable temperature effect. It is concluded that the long-lived excitation is metastable electronic molecular states.

There are three possible metastable states in N_2 : $A^3\Sigma_u^-(6\text{ eV})$; $^3\Delta_u(7\text{ eV})$; and $^1\Delta_u(9\text{ eV})$; and three in oxygen: $^1\Delta_g(1\text{ eV})$; $^1\Sigma_g^+(2\text{ eV})$; and $^3\Sigma^+(4\text{ eV})$. The nitrogen states have lifetimes of ≈ 1 sec and the oxygen ≈ 10 sec. All can be produced by free radical recombinations or electron impact, or excitation transfer from other atoms. To produce

the visible light output of the ball, at least 10^{17} atoms/cc or 1% of the gas must be in the excited state. Losses to impurities and radiation in the nonvisible spectrum may require a greater fraction of excitation.

Experiments are being carried out to discover what species are present and how they are produced.

MHD Applications

Three possibilities exist for producing ionization in an MHD generator from states excited by fission fragments:

where N_2^* = electronically excited nitrogen and N_2^{**} = vibrationally excited nitrogen.

Reaction (3) is equilibrium controlled, and the rest are rate controlled. Fission fragment bombardment produces N atoms with better than 50% efficiency; N_2^* and N_2^{**} are produced by the recombination of N atoms. All the above reactions have been observed experimentally and the rates are known within an order of magnitude.

If reaction (1) is to be used, then the MHD generator expansion must be a constant atom density expansion, otherwise ionization would vary too greatly along the channel. Figure 14 illustrates the conductivity achievable with 5% of the total energy deposited in the gas as free N atoms.

A more practical approach, not requiring a constant density expansion, is by using reactions (2) and (3). By using relatively high pressures (e.g., 5 atm) all excitation energy can be degraded to vibrational energy. As the gas density drops the vibrational temperature remains "frozen" and conductivity will be constant along the generator. Such frozen equilibrium has been observed to last in shock waves for many milliseconds.

It is planned to seed the long-lived rf discharges in nitrogen and in nitrogen plasma torches with cesium, and measure the magnitude and relaxation rate of conductivity. Fission fragment induced conductivity will also be measured.

THERMAL EQUILIBRIUM URANIUM HALIDE PLASMAS

Theoretical studies show that at temperatures above $2500^\circ K$ uranium halides like UBr_4 and UI_4

Figure 14. Conductivity vs pressure for chem-ionized gas.

Figure 15. Current output *vs* time for two different slug lengths in experimental generator.

Figure 16. Input mechanical and output electrical power *vs* time.

Figure 17. Generator efficiency *vs* slug length for different external loads.

will be dissociated and ionized sufficiently to provide useful plasma conductivities. Experimental tests of the conductivity will be required.

Liquid Metal Slug MHD Generator

The liquid metal slug MHD generator is a channel with a transverse magnetic field. Slugs of liquid metal (e.g., potassium) are injected at the high pressure end (e.g., 400 psia) of the channel, and expanding metal vapor pulses the slug through the field. The expansion energy is converted directly to electricity. Electrodes at the sides of the channel connect to the load. Potential advantages are relatively low liquid velocities (100 ft/sec), high cycle efficiencies ($>20\%$), generation of 60-cycle ac which can be transformed to load conditions, and an extremely light compact generator [0.5 lb/kW(e)].

A single slug mercury generator was tested over a wide range of magnetic fields, slug lengths, driving pressure, and load resistance. It delivered a maximum of 2 kW (2000 amp at 1 V) of 50-cycle ac. The absolute efficiency was low (only 10 to 15%) because of the high density of mercury, and most of the expansion energy appeared as kinetic energy of the slug. When actual output was compared to that predicted using measured slug velocity, field, and load resistance, the actual efficiency was 60%.

Three to four-in. slugs traveled 2 ft before they broke up and were penetrated by the driving gas. Six-in. potassium slugs should travel at least the 4-ft length of the design generator.

Figure 15 shows the effect of slug length on current output. The short slug accelerates quickly but only travels past the first two electrode pairs before breakup. The long slug travels the active generator length (2 ft) before breakup; however, it is longer than the interelectrode length for the first couple of electrode pairs and its current is short-circuited. A practical compromise seems to be a slug some 30% longer than the interelectrode length.

Figure 16 compares the generated power and predicted power with the actual power input. As mentioned previously, most of the input goes into kinetic energy of the slug. The generated power is zero when the slug commutates between electrodes, and then rises to the predicted value when centered on the electrode pair. A larger channel would bring the generator efficiency even closer to predicted values while the low density of the potassium working fluid in the projected generator will eliminate loss to slug kinetic energy.

Figure 17 shows the measured efficiency as a function of slug length and load resistance. Except for very low resistance, it is about 60% until the slug length becomes so large that short circuits reduce power output.

A new single slug generator of approximately the same cross section but 3 ft long is being constructed. It will test 6-in. NaK slugs and should show a real efficiency $>60\%$.

Rayleigh-Taylor MHD Stability Studies

One of the most important problems in the liquid metal MHD generator is slug stability. The high pressure slug surface is subject to a destabilizing body force that produces an ever growing wave. When the wave grows sufficiently to penetrate the slug, gas can blow through and further generation is impossible. In an extensive series of experiments, this effect was tested, both in the hydrodynamic regime where fluid inertia effects are predominant, and in the hydromagnetic regime where magnetic effects are predominant.

For hydrodynamic effects, an experiment was made on water slugs accelerated by high pressure gas. Growth rates of short wavelength instabilities (shorter than container dimensions) agreed with those predicted by theory, i.e., an exponential growth of amplitude with the exponential time constant

$$n = (gk)^{1/2}$$

and a change to a nonlinear constant velocity solution when amplitude was comparable to k^{-1}

$$V = (g/k)^{1/2}.$$

The nonlinear solution was obtained in the course of this work.

The hydromagnetic instability growth rate was then predicted and tested experimentally. An initial exponential growth of the amplitude was found with

$$n = \frac{g^{2/3} \rho^{2/3} k^{2/3}}{B^{2/3} \sigma^{1/3}},$$

where g = acceleration, ρ = density, k = wave number, B = magnetic field, σ = conductivity, and a subsequent nonlinear growth at amplitudes $>k^{-1}$ of $V = \rho g / \sigma B^2$. The nonlinear solution was obtained in the course of this work.

So far, only the nonlinear region has been experimentally accessible, but a constant velocity growth has been observed within 20% of theory and is a factor of ten lower than predicted by ordinary hydrodynamic theory.

More experiments will be made with cleaner systems in which the linear region can be observed.

Figure 18. Reciprocating solid slug MHD generator.

Solid Slug MHD Generator – MHD Bearing

Delays in the start of construction of this device have led to beneficial changes in design. A simplified isometric view is shown in Figure 18. The laminated piston, lubricated by liquid metal forced into pressure pad bearings, is driven in reciprocating motion through the magnetic field by gas through high capacity valves mechanically actuated by the piston. Alternating current is taken from bus bars, one of which terminates in a direct contact to one side of the piston, the other of which goes through conductors over and under the piston (forming two walls of the cylinder) to the contact for the other side of the piston. This arrangement of conductors minimizes the circuit inductance. Electrical contact is made to the piston via the liquid metal lubricant. Insulation on appropriate surfaces prevents short circuits except through the thin film of metal lubricant on the top and bottom surfaces.

The device is intended to be a prototype of a Rankine cycle device utilizing alkali metal vapor at higher temperatures than those that can be utilized by turbines. The relative simplicity and low speed of the device compared to a turbine, with no disadvantage in power-to-weight ratio, will make it especially suitable for space power. The present model is meant to operate at room temperature but will test the magnetohydrodynamic liquid metal lubrication system demanded by a full scale machine. Construction on the model has just started.

CLOSED CYCLE ELECTROCHEMICAL CONVERTER

Work is continuing on the development of the lead bromide converter. The device, which consists of two electrochemical cells of the type $\text{Pb(l)} | \text{Pb-Br}_2(\text{l}) | \text{Br}_2(\text{C})$ and an interposed heat exchanger, operates with the electrolysis cell at 900°C and the continuous feed primary cell at 370°C . Such a con-

verter would be especially appropriate if used in conjunction with a reactor cooled by liquid lead. The coolant could then be circulated directly to the high temperature cell, thus avoiding an intermediate heat exchanger. A literature search was performed specifically to review available data relating to the use of liquid lead as a reactor coolant. Primary emphasis in laboratory experiments has been placed upon materials testing and cell development.

Materials Testing

Continued testing of silica glass with lead, lead bromide, and bromine at 900°C has shown no evidence of corrosion. The methods used to measure corrosive effects were microscopic and metallographic examination, and visual observations. Table 6 summarizes the conditions in isothermal static tests.

The following ceramic materials were tested in bromine at 900°C for periods in excess of one day: SiC , ZrC , TiB_2 , ZrB_2 , MoSi_2 , Si_3N_4 , AlN , BN , and ZrO_2 . Of these, only SiC and ZrO_2 are resistant to bromine. The criterion for corrosion resistance is less than one milligram weight change in a several gram sample.

A specimen of spectrographic grade graphite was immersed in liquid lead in a silica glass capsule with hydrogen gas present, and 500 hr were accumulated at 900°C . There was no apparent interaction of any kind. The weight of the 3.7575-g sample decreased by 0.0014 g.

A test of the general compatibility of graphite with bromine was performed at 900° for 66 hr. Three specimens weighing nominally 1, 2, and 3 g were used. The greatest apparent weight loss was <2 mg. Numerous 24-hr tests of the uptake of bromine by graphite were performed. Three specimens of graphite were used, one spectrographic grade, the other two type AUC. Bromine was supplied at a pressure of 4 psig. No change in weight or dimensions was found at temperatures $\geq 150^\circ\text{C}$.

Table 6

Isothermal Tests of Silica Glass

Substance	Temperature, $^\circ\text{C}$	Time, hr	Remarks
$\text{SiO}_2\text{-Pb}$	900	2000	Hydrogen atmosphere
$\text{SiO}_2\text{-Pb-PbBr}_2$	900	500	Argon atmosphere
$\text{SiO}_2\text{-Br}_2$	900	200	—
$\text{SiO}_2\text{-Pb-PbBr}_2\text{-Br}_2$	900	200	—

Cell Development

A test of a single electrolysis cell with lead and bromine electrodes to determine current and energy efficiency and to examine polarization phenomena was recently completed. The silica container was in excellent condition after two-months' exposure to the effects of electrolysis in this system at temperatures which were varied from 500° to 900°C. The gas liberated during electrolysis with a graphite (type AUC) electrode at current density up to 1.5 A/cm² was bromine only with no compounds of carbon formed as a result of electrolysis. No erosion or swelling of the graphite electrode was found in postexperiment examination. The carbon electrode was thus unaffected by contact with the molten salt as well. The rate of bromine pressure decline on open circuit was measured at a series of temperatures. Over-all reaction rate data obtained from this and previous experiments with different cross sectional areas are plotted *vs* the reciprocal temperature in Figure 19. The insensitivity of reaction rate to salt thickness suggests the reaction rate may be controlled by free convection. In the current experiment, it was found that a small addition of NaBr (0.27 wt %) had no effect on the reaction rate. J. McNICHOLAS, J. POWELL, M. TAVEL, M. ZUCKER

Evaluation and Technical Assistance Group

L. GREEN

DESIGN AND EVALUATION STUDIES

Economics of a Lead Bromide Direct Conversion System

An economic study was made of the use of a lead bromide chemical direct conversion device as a topping unit for a 1000-MW(e) nuclear power plant. The cell operates at temperature extremes of 400° to 900°C, and produces low voltage dc power. The thermodynamic efficiency of the binary system is 60%, compared to 40% for a standard power generation system. It was concluded that the system can be economical if current densities of the order of 2000 amp/ft² can be achieved, and if cells and auxiliary equipment can be fabricated for ≈\$14/ft². In addition, the problem of converting low voltage dc power to high voltage ac for transmission in this system is an important one,

Figure 19. Bromine-lead reaction rate.

and it was therefore suggested that the system be considered for use in the metallurgical refining industries where low voltage dc power is consumed at a high rate. The ac power block from the binary system could then be transmitted by conventional methods.

The study thus points up the need for extensive engineering work to bring the system to a point of practical use. The feasibility of producing high current densities must be established, and low cost electrodes developed to reduce cell investment costs to a level competitive with conventional power generation equipment. M. BELLER, L. GREEN

Remote Rotor Electric Drive

At the request of the AEC, New York Operations Office, a proposal for developing a remote rotor electric drive for hermetically sealed cooling systems in nuclear powered reactors was reviewed considering the electrical engineering aspects of the rotor drive. The drive was evaluated for use in a seal-less sodium pump (50,000 to 100,000 gpm). This proposal has been reviewed by various BNL staff members and a report was submitted to NYOO. L. GREEN

Super Temperature Dual (STD) Flow Turbine System

At the request of the Systems Analysis Branch, the proposal to apply the STD principle to nuclear/chemical plants was reviewed. The findings and conclusions of the BNL staff involved in the review have been summarized in a report to the

AEC. This report presented a description of the concept, showed its application to nuclear systems, compared the thermodynamic advantages to the disadvantages necessitated by the practical utilization of the concept, and pointed out alternative schemes under study and in use to accomplish the same purpose. L. EPEL, L. GREEN

NUCLEAR COST GUIDE

Revision of the chapters on capital costs and operation and maintenance costs of the Nuclear Cost Guide was completed and a preliminary draft was submitted to the Reactor Evaluation Staff, OAGMR. Burns & Roe assisted in the revision of the Nuclear Cost Guide under the terms of their current contract. The chapters on capital costs and operation and maintenance were reviewed considering (1) a maximum unit plant size of 5000 MW(t), (2) the latest general costing practices for nuclear plants, and (3) changes that should be affected because of hot experience gained since the issue of the Cost Evaluation Handbook (TID 7025) in 1962. Oak Ridge National Laboratory has the primary responsibility for preparation of the Nuclear Cost Guide and will complete the remaining chapters. L. GREEN

NUCLEAR SAFETY PROGRAM REVIEW

A review paper entitled Evaluation of the Research and Development Programs Related to SNAP Reactor Fuel Element Burnup and Resultant Particle Size Distribution Upon Hypersonic Velocity Re-entry Into the Earth's Atmosphere by M. Maresca and L. Green was submitted to the Office of Program Evaluation, in connection with the review of the Aerospace Safety Program. The purpose of this study was to review the R&D Programs which are developing data on the ultimate fate of SNAP reactor fuel elements and SNAP isotopic generators upon re-entering the earth's atmosphere from a space environment either by design or accident. The information presented was based on a comprehensive review of the available reports and information obtained from visits to the major contractors working in this area. Visits included the Sandia Corporation, Atomics International, Cornell Aeronautical Laboratory, and the Martin Company. This report essentially completes BNL's work on the Nuclear Safety Program Review. M. MARESCA, L. GREEN

TRANSURANIUM ELEMENTS

The production of heavy elements such as Pu^{238} and Cm^{244} by multiple neutron capture in uranium and plutonium fuel has been studied. The salient feature of the studies was the utilization of neutrons in the resonance energy range (epithermal) rather than thermal neutrons. The advantages of using an epithermal irradiation flux over a thermal one are due to the behavior of the capture and fission cross sections as functions of neutron energy. It happens that over-all there is an increase in neutron capture rates compared to fission for the nuclide chains involved as the neutron spectrum becomes hardened. Thus a given amount of product can be made more quickly and economically if the raw material is subjected to an epithermal neutron flux.

This proposition has been tested with two computer programs designed for the purpose. In all cases the superiority of epithermal irradiation over thermal irradiation has been established.

In the first, less sophisticated code, PLUCAL, fission, capture, and beta decay for the nuclides in the main production path were considered. The linear first-order differential equations describing the buildup of these isotopes were solved for various ratios between the epithermal flux and the thermal flux. A number of conceptual fuel management schemes were studied, as were a number of specific powers, appropriate to the degree of epithermality being used.

The second program, PUPER, designed for the Pu^{238} production chain, takes into account alpha decay, electron capture, $(n,2n)$, and $(n,3n)$ reactions in addition to the processes considered in PLUCAL. Furthermore, the time dependent inventories of nuclides not in the main production path are computed since they enter into the Pu^{238} production scheme also. Rather than keeping the ratio of epithermal flux to thermal flux constant, however, PUPER allows for a shift in the neutron spectrum as various isotopes build up in the system. In PUPER, the physical model which determines the neutron spectrum dictates that the epithermal flux is inversely proportional to the resonance escape probability and the moderating ratio of the system. Thus at every time step during the numerical integration of the set of differential equations, the resonance escape probability and moderating ratio are computed from the nuclide inventories and the appropriate cross sections and resonance integrals. These in turn yield the ratio

of epithermal to thermal flux and thus the nuclear reaction rates for the next time step are calculated.

Again, as in PLUGAL, all results indicate that there are advantages in using a hardened spectrum for Pu^{238} production by multiple neutron capture.

A more sophisticated code, which is an extension of PUPER, is being prepared. It does what PUPER does but calculates an *effective* resonance integral from resonance parameters (which are input to the program) and computed inventories. It then uses these effective resonance integrals rather than the infinite dilution resonance integrals for computing the reaction rates in the epithermal group.

L. EPEL, J. CHERNICK

MODIFICATION OF POWER REACTOR CONTROL RODS TO PRODUCE SALABLE Co^{60}

A study is being made to determine the feasibility of substituting Co^{59} for some of the other structural materials normally used in the fabrication of control rods. The reactor design and operation are not altered with this substitution. Two criteria used to establish equivalence between the currently conceived control rod characteristics and the modified Co^{59} control rod are blackness and control rod life. In effect, the rod blackness of the modified control rod must remain as black as the original over the life of the rod.

A materials substitution is made in a typical power reactor control rod. Stainless steel structural materials within the protective stainless steel shroud are replaced with blacker Co^{59} . In all, 33.3% of the available internal volume of the modified control rod is Co^{59} .

The results of the activation analysis indicated that significant quantities of high specific activity Co^{60} would be produced. M. MARESCA, L. GREEN,

L. EPEL, B. MANOWITZ

POLONIUM PRODUCTION BY BISMUTH IRRADIATION

Modifications have been made to the REPETITIOUS code for obtaining resonance absorption rates in Bi. An investigation will be made of the effect of varying resonance parameters. Analytical calculations of the resonance integrals are also being made.

Preparation has been started for obtaining cross sections of Bi for use in multigroup calculations of

reaction rates in mixed spectra. Calculations of mixtures of fast plus thermal spectra are required. These have been treated successfully in criticality calculations by the Los Alamos multigroup library of Hansen and Roach. The Bi multigroup cross sections are being prepared for use with this cross section library. M. LEVINE, A. ARONSON

ROTATING FLUIDIZED BED RESEARCH REACTOR

An examination of the rotating fluidized bed reactor concept proposed by L.P. Hatch and associates at BNL, indicated that this reactor could produce extremely high fluxes for significant time periods. The essential feature of this system is the use of a particulate fuel in the form of a rotating annular bed fluidized by a coolant gas and constrained in the core by centrifugal force. Physics and mechanical design studies indicate that it may be feasible to build a reactor of reasonable size with rather conventional auxiliary equipment, and to obtain fluxes in the order of 4×10^{16} neutrons/cm² sec at 5000 MW(t) for a period of ≈ 1 min. Fluxes of this type are an order of magnitude higher than that obtainable from recently built high flux research reactors.

The physical model studied consisted of four adjacent regions containing in order, superheated light water steam, a fuel annulus, a porous zirconium shell, and a heavy water reflector. This one-dimensional spherical system was studied with both a multigroup diffusion code and a multigroup transport code, and good agreement was noted between the two methods. The critical mass was found to be essentially independent of the choice of U^{233} or U^{235} as fuel or of the fuel annulus size over the range investigated. Since the fuel inventory is low, extraordinary neutron flux levels are possible at the design power level of 5000 MW(t). Figure 20 shows the thermal neutron flux distribution with a broad peak at 4×10^{16} neutrons/cm².

A schematic flow diagram of the reactor system is shown in Figure 21. The indicated process conditions are for a steam cooled reactor; however, other gas coolants could also be used.

The rotating reactor core is cylindrical, 4.5 ft in diameter by 4.5 ft long. Coolant flows radially inward from the periphery of the cylindrical core through a porous structure, fluidizes the bed, and exits through a nozzle at one end of the cylinder. In the settled condition, the $\text{UO}_2\text{-ZrO}_2$ fuel particles form a bed 1 in. deep. The core rotates at

about 3000 rpm and is surrounded by a heavy water reflector. An extremely high power density is attained because of the excellent heat transfer characteristics of the bed.

For the purpose of this study, a one-minute operating time was assumed with at least a one-hour shutdown between runs. This operating cycle results in conventional auxiliary systems and components.

The use of a condensable working fluid permits high-pressure storage of the coolant in the liquid state thus minimizing the size of the vessels. Pumping power is also reduced by condensing the effluent prior to pumping it back to the high-pressure storage vessel. The high temperature superheated exhaust from the reactor is utilized to vaporize the inlet coolant since the coolant enters the core as a saturated vapor.

Most of the auxiliary equipment is conventional, hence the capital cost of this system is similar to that of a large water-cooled nuclear power plant. The reactor cost is difficult to estimate because of the added mechanical complexity of the rotating core. The feasibility of the Rotating Fluidized Bed Reactor for space applications is currently being studied at BNL. Experiments are being performed to determine bed stability, bed hydraulic characteristics, and bed heat transfer properties.

K. HOFFMAN, L. EPEL, L. GREEN,
J. CHERNICK

Figure 20. Thermal neutron flux distribution at 5000 MWt.

Sigma Center

J. STEHN

NEUTRON CROSS SECTION COMPILATION GROUP

Volume III of the second supplement to BNL 325, Second Edition, was completed in May and sent to the printers. Distribution of copies to recipients listed on the Sigma Center distribution list was completed in August. This volume displays the measured cross section values for nuclei with $Z=88$ to 98 for which significant new information has become available since the publication in 1960 of the first supplement.

Work began in August on the preparation of Volume II to the second supplement. This will complete the table of nuclides, covering the region $Z=21$ to 87. It is anticipated that this volume will be available for publication by Summer-Fall 1966.

At the request of Dr. Katherine Way of Oak Ridge, a collaborative agreement was reached whereby the Compilation Group will provide the neutron resonance parameters needed by the Nuclear Data Group for publication in the Nuclear Data Sheets. Parameters for nuclei in the region $A=180$ to 190 have been prepared and submitted to the Oak Ridge group.

The data tape SCISRS, which contains a listing of all experimentally measured cross section values,

Figure 21. Flow diagram of rotating bed research reactor.

now has over 200,000 points. All new data received by the Group are immediately put into the SCISRS format. The present tape contains essentially all data for the fissionable materials and a rather complete listing for the $Z=1$ to 20 nuclei. All angular distribution data should be included by the end of 1965. Completion of the listing of old data for $Z=21$ to 87 will proceed parallel with the work on Volume II of the supplement.

The collaborative program on SCISRS with the Neutron Data Compilation Group (located at Saclay) of the European Nuclear Energy Agency should be in full working order by the beginning of 1966. Through this program all new experimental data obtained in the ENEA member countries will be put into SCISRS by the Saclay group.

M. GOLDBERG, J. STEHN, R. WIENER-CHASMAN,
S. MUGHABGHAB, L. HJÄRNE,
B. MAGURNO, V. MAY

REACTOR CROSS SECTION EVALUATION GROUP

Single Level Fitting of the Cross Section Curves

The contribution of each observed resonance to the neutron cross section has been calculated using the Breit-Wigner single level formula. Total and partial cross sections as a function of energy were generated by a simple superposition of the contributions made by individual resonances. The resultant cross section was Doppler broadened and interference between resonance and potential scattering included.

The cross section data of BNL 325 was used to determine the agreement between the cross section derived from the resonance parameters and the monoenergetic, differential, and integral measurements. The study considered several isotopes in the range from Mn^{55} to Cm^{246} , and showed the single level formula to be a useful tool for testing the consistency between differential and integral measurements and for providing new information.

Evaluated Nuclear Data File

A new evaluation by KAPL of the fast neutron cross sections for oxygen has been added to the ENDF Master Library which already includes the Aldermaston/Winfrith data file. Conversions to the ENDF format are in progress for the Bettis ROC system, Atomics International Evaluated Nuclear Data File, and the Battelle-Northwest RBU data. A report describing the service rou-

tines, which have been completely rewritten, will be available soon.

Cross Section Fluctuations

The problem of nuclear cross section fluctuations in the continuum region is being analyzed theoretically using a random matrix approach. Dyson's ensemble of unitary symmetric matrices, originally introduced for the purpose of deriving energy level distributions, is generalized in the present application to include nonuniform eigenvalue distributions on the unit circle. One important advantage of the matrix ensemble method is that the results are invariant to any change in channel labeling scheme. Associated numerical work involving the generation of random orthogonal matrices is also proceeding.

The Scattering Cross Section of Sodium

An analysis of the scattering cross section of sodium from thermal energy to the 2.85-keV resonance is in progress. The cross section has been tracked experimentally throughout this region and provides an excellent guide for the analysis. The 2.85-keV resonance appears to be responsible for the cross section throughout this region and the analysis therefore utilizes the single level Breit-Wigner resonance formula. The analysis also utilizes scattering lengths extracted from coherent scattering and total scattering cross section measurements. The absorption and scattering resonance integrals have been calculated.

Optical Model Calculations

Good agreement with the inelastic and elastic neutron scattering data on aluminum and iron was obtained from optical model calculations using a complex, spin-dependent, diffuse-edge, spherical potential with surface absorption. The data could be fit over an energy range of about 1 to 5 MeV using energy independent parameters.

Reactor Cross Section Evaluation *Newsletter No. 8* [BNL 904 (N-8)], reporting optical model calculations for sodium, was issued describing preliminary results of a group headed by P.F. Zweifel and M. Shur under a subcontract with BNL. Good fits to the elastic and inelastic scattering neutron data in the 1 to 4-MeV energy range were obtained, indicating that the optical model is useful for studying light nuclei.

T. KRIEGER, S. MOORE, S. PEARLSTEIN,
T. STEPHENSON, H. HONECK

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HIGH TEMPERATURE THERMODYNAMICS

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Thermodynamics of Fused Salt Systems by Electromotive Force Measurements – The Binary Systems of KCl With MgCl₂, CaCl₂, and SrCl₂

Electromotive force measurements on cells using only gaseous electrodes were employed to obtain thermodynamic properties of molten KCl mixtures.

When a wide variety of systems is studied, metal electrodes often introduce difficulties. Since many salts dissolve their own metals with ensuing electronic conductivity imparted to the melt, the cell is "shorted out" and the measured emf's are not the intended equilibrium values. Also, mixtures of salts whose free energies of formation are close together cannot generally be studied because of displacement reactions that take place at the metal electrode.

Cells of the following type were employed in this work.

In cell (I) the over-all reaction on passing one Faraday of electricity is

so that

$$F_{\text{KCl}}^{\text{M}} = -\mathcal{F}E$$

where $F_{\text{KCl}}^{\text{M}}$ is the relative partial molar free energy of KCl, $\mathcal{F}$ the Faraday, and E the emf of the cell.

The glass is a special K⁺ selective glass described by Portnoy, Thomas, and Gurdjian [*Talanta* 9, 119

(1962)]. Since the softening point of the glass is just above the melting point of KCl, cells of type (II) were used to operate at temperatures lower than the melting point of KCl.

Results were obtained over the entire composition range for the binary systems KCl-MgCl₂, KCl-CaCl₂, and KCl-SrCl₂. In general, large negative deviations from Raoult's law were observed. Values of the free energies of mixing, the excess free energies of mixing, and the activities for KCl are given in Tables 1, 2, and 3. Figure 1 shows the activities of KCl plotted against composition for the three systems.

Thermodynamics of the Uranium-Carbon System

The free energy of formation of uranium sesquicarbide was determined by means of the solid state cell

The over-all cell reaction on passing six Faradays of electricity is

The free energy of formation is then given by

$$\Delta F_{\text{U}_2\text{C}_3}^0 = -6\mathcal{F}E.$$

The emf results are shown in Figure 2 in comparison with those obtained with UC₂ as reported previously [BNL 900 (S-67)].

The U₂C₃ was prepared by heating U and UC₂ at 1450°C for 35 hr under vacuum. Uranium powder and UC₂ powder were mixed under carbon tetrachloride, pressed into pellets, and then heated in an induction furnace. The pellets were crushed and re-pressed at time intervals of 5, 12, and 18 hr.

The free energy values for UC₂, U₂C₃, and UC₂ are shown in Figure 3. The value of UC is taken from the literature. It can be seen from this diagram that U₂C₃ is the stable phase in equilibrium with C at these temperatures. Even though this is the case, it was possible to operate the cell

Table 1

Thermodynamic Properties
of KCl-MgCl₂ Mixtures at 725°C

x_{KCl}	$-F_{\text{KCl}}^M, \text{ cal}$	$-F_{\text{KCl}}^E, \text{ cal}$	a_{KCl}
0.10	13,350	8,785	0.0012
0.20	10,840	7,650	0.0042
0.30	8,830	6,445	0.0116
0.40	7,080	5,265	0.0281
0.50	5,375	4,000	0.0665
0.60	3,780	2,765	0.149
0.70	2,100	1,395	0.347
0.80	920	475	0.630
0.90	200	90	0.90

Table 2

Thermodynamic Properties
of the KCl-CaCl₂ System at 785°C

x_{KCl}	$-F_{\text{KCl}}^M, \text{ cal}$	$-F_{\text{KCl}}^E, \text{ cal}$	a_{KCl}
0.10	9295	4455	0.012
0.20	7030	3650	0.035
0.30	5515	2985	0.073
0.40	4245	2315	0.133
0.50	3205	1750	0.218
0.60	2190	1115	0.353
0.70	1360	610	0.524
0.80	740	270	0.704
0.90	300	65	0.87

Table 3

Thermodynamic Properties
of the KCl-SrCl₂ System at 750°C

x_{KCl}	$-F_{\text{KCl}}^M, \text{ cal}$	$-F_{\text{KCl}}^E, \text{ cal}$	a_{KCl}
0.20	4820	1550	0.093
0.30	3830	1385	0.147
0.40	3000	1135	0.228
0.50	2285	875	0.325
0.60	1685	645	0.436
0.70	1130	405	0.574
0.80	670	215	0.720

Figure 1. Dependence of the activity, a , on the mole fraction, x , of KCl in the binary systems KCl-SrCl₂, KCl-CaCl₂, and KCl-MgCl₂.

Figure 2. Emf values of the cells U, UF₃|CaF₂|UF₃, UC₂, C and U, UF₃|CaF₂|UF₃, U₂C₃, C.

Figure 3. Relative integral molar free energy in the system uranium-carbon.

Figure 4. Experimental cell used for the study of metal-metal halide systems.

Figure 5. The relation between Pb activity and the product $i_0 \tau^{1/2} / (i_0 \tau^{1/2})_{a_{\text{Pb}}=0}$ due to subhalide in PbCl_2 . Curve A corresponds to the formation of Pb^+ and curve B corresponds to the formation of Pb_2^{+2} .

because of the very slow transformation of UC_2 to U_2C_3 and C at 900°C .

Metal-Metal Salt Solutions

Studies were continued on the dissolution of metals in their salts. By using a chronopotentiometric technique [BNL 900(S-67)], the Ag-AgCl, Ag-AgBr, Pb-PbCl₂, and Zn-ZnCl₂ systems were studied. Figure 4 shows the experimental cell developed for use with all these systems.

Additional data were obtained on the Ag-AgCl system. It was found that iridium metal was the most satisfactory electrode material for all the systems studied including the Ag-AgCl system. At 520°C , it was found that silver dissolves in its chloride to the extent of 0.0123 mole % and that the diffusion coefficient for the soluble silver species was $2.0 \times 10^{-5} \text{ cm}^2/\text{sec}$. Analysis of the chronopotentiometric wave shapes (see BNL 900) showed that the oxidation process was a reversible one-electron step.

The solubility and diffusion coefficients of silver dissolved in its bromide at 500°C were determined to be 0.0118 mole % and $4.2 \times 10^{-5} \text{ cm}^2/\text{sec}$, respectively.

The lead-lead chloride and the zinc-zinc chloride systems were studied using the chronopotentiometric techniques used for the Ag-AgCl system (BNL 900) and the Mg-MgCl₂ system [BNL 782 (S-63)]. The solubilities of lead and zinc in their chlorides were found to be 0.0057 mole % for lead in lead chloride at 518°C , and 0.019 mole % for zinc in zinc chloride at 500°C . By measuring the concentrations of dissolved metal as a function of metal activity in a metal alloy in contact with the salt (see BNL 782), it is possible to differentiate between the two possible modes of dissolution of lead and zinc in their chlorides:

or

According to the law of mass action, the concentration of dissolved metal will vary as the square root of the metal activity in a contacted metal alloy for reaction (I) while there will be a direct dependence for reaction (II). Thus a plot of $i_0 \tau^{1/2} / (i_0 \tau^{1/2})_{a_{\text{M}}=1}$ will be a straight line for reaction (II) and a curve for reaction (I). This arises from the

fact that the product $i_o\tau^{1/2}$ is directly related to concentration:

$$i_o\tau^{1/2} = (nF\pi^{1/2}D^{1/2}C)/2. \quad (\text{III})$$

Figure 5 shows such a plot for the dissolution of lead in its chloride at 518°C. A similar plot is obtained for the zinc-zinc chloride system at 500°C.

This shows that zinc and lead dissolve in their chlorides according to reaction (II). The diffusion coefficients of these ions were calculated to be 1.8×10^{-5} cm²/sec for Pb_2^{+2} at 518°C, and 7.6×10^{-6} cm²/sec for Zn_2^{+2} at 500°C.

It was found that rigorous purification of the salts was essential in these studies. The lead chloride was purified by passage of HCl gas over powdered lead chloride and subsequently through liquid lead chloride to remove traces of water. Chlorine gas was later passed through the liquid lead chloride and the final purification step was to equilibrate the liquid lead chloride with gold to remove traces of dissolved lead.

Zinc chloride was made by passing HCl gas over zinc metal at 700°C and distilling the zinc chloride under this stream of HCl. The zinc chloride was later subjected to a stream of chlorine gas while molten, and the final purification step was the contacting of the pure zinc chloride with pure bismuth metal to remove traces of dissolved zinc. Elaborate care had to be used in handling the zinc chloride as it is extremely hygroscopic.

THERMODYNAMIC STUDIES OF UI_3

J. TVEEKREM, R. WATSON

The free energy of formation of UI_3 has been determined by measuring the emf of the solid state cell $\text{U}, \text{UI}_3 | \text{NaI} | \text{AgI} | \text{Ag}$. The three best available literature values for the free energy of formation of AgI were averaged and this value was combined with the cell emf data to give the ΔF_f of UI_3 at 320° and 370°C. The respective values thus obtained were -102.2 ± 0.6 and -99.0 ± 0.6 kcal/mole. These values were ≈ 6 kcal/mole more positive than the estimated values in the literature.

OPTICAL SPECTRA OF FISSION PRODUCTS

J. TVEEKREM, R. WATSON

Attempts to study the absorption spectrum of gaseous UI_3 were discontinued when it was discovered that the UI_3 decomposed on contact with the quartz cell at temperatures above 450°C. Mo-

lecular iodine was liberated which gave a broad absorption in the visible that was mistakenly ascribed to UI_3 in the previous annual report. The absorption decreased with increasing temperature in consort with the dissociation of molecular iodine, and increased absorption occurred when the temperature was lowered and the iodine dissociation equilibrium reversed. This inverse temperature effect on the absorption also indicated that the decomposition of UI_3 was not reversible. The uranium was apparently stabilized as UO_2 .

FLUOROCARBON STUDIES

D. MACKENZIE, J. FAJER, F. BLOCH, D. RIEL

Perfluoroaromatics

It was previously reported (BNL 900, p. 33) that perfluoronaphthalene irradiated at 450°C gave a large yield of fragmentation products in contrast to perfluorobiphenyl and perfluoro-*o*-terphenyl. This was based on the short GLC retention times of the two main products compared to that of parent C_{10}F_8 , and on the rather high volatility one would expect from such short retention times. Attempts to determine molecular weights by vapor density measurements were unsuccessful because of the small amounts of the compounds which had been isolated.

A subsequent irradiation produced sufficient amounts of the compounds for identification. Molecular weights have been determined with a mass spectrometer and these are being checked by vapor density measurement. The two compounds, one a colorless liquid and one a clear crystalline solid, have the same molecular weight, corresponding to $\text{C}_{10}\text{F}_{10}$, although both are considerably more volatile than C_{10}F_8 .

Since the mass spectra of the two compounds are very similar and resemble that of perfluorostyrene, it is probably that they are due to the *cis*- and *trans*-isomers of perfluorobutadienylbenzene. However, in order to characterize the compounds unequivocally, NMR studies will be carried out along with the IR investigation now in progress.

No conclusions can be drawn regarding the radiolysis mechanism until the structures of the $\text{C}_{10}\text{F}_{10}$ products are known definitely. It is clear, however, that in spite of their high volatility these particular compounds are addition products rather than fragmentation products. In fact, the yield of true fragmentation products is really quite

small, in line with the results obtained with the other aromatics.

Perfluoroalicyclics

Perfluorobicyclohexyl, $C_{12}F_{22}$, had been irradiated at 450°C in order to compare its behavior with that of the analogous aromatic compound perfluorobiphenyl, $C_{12}F_{10}$ (BNL 900, p. 33). While the aromatic showed surprising stability, the alicyclic showed an unusually high G -value, >200 , for loss of starting material. Further experiments have shown this G -value to be in fact very much higher – of the order of 2×10^5 . This reaction thus proceeds by a chain of great length, the first example of a chain reaction that has been found in the fluorocarbons.

Since $C_{12}F_{22}$ was not necessarily typical of alicyclic fluorocarbons, other alicyclics shown in Table 4 were purified by preparative scale GLC and irradiated at 450°C to a dose of 78 megarads. The results are summarized in Table 4 along with those of pyrolysis experiments carried out in parallel. They show that $C_{12}F_{22}$ is the only compound whose radiolysis proceeds by a chain reaction. All the other compounds irradiated were almost as stable as the aromatics. The single ring compound,

Table 4

Radiolytic and Pyrolytic Decomposition Yields
in γ Irradiation of Alicyclic Fluorocarbons
at 450°C . Dose, 78 megarads in 10 hr.

Compound	Wt % decomposition		G_{total}^a	$G_{\text{radiolytic}}^b$
	Total	Pyrolysis		
F-cyclobutane, C_4F_8	7.5	negligible	4.6	4.6
F-cyclohexane, C_6F_{12}	8.2	0.7	3.4	3.1
F-naphthalene, $C_{10}F_{18}$	25.4	1.9	6.8	6.3
F-phenanthrene, $C_{14}F_{24}$	50.1	6.4	9.9	8.6
F-fluoranthene, $C_{16}F_{26}$	44.2	7.4	7.9	6.6
F-bicyclohexyl, $C_{12}F_{22}$	82 ^c	5.4 ^c	$\approx 2 \times 10^5$	

^aAll G -values refer to molecules at starting compound destroyed per 100 eV of energy absorbed in the system.

^b G_{total} corrected for pyrolytic decomposition.

^cTotal dose, 7.4×10^3 rads; irradiation time, 20 min.

C_6F_{12} , is really quite remarkable for an alicyclic structure. Its total radiolytic decomposition yield is lower than that of the aromatics $C_{10}F_8$ and $C_{18}F_{14}$, which is in striking contrast to the behavior of alicyclic hydrocarbons. The fused ring, perfluoronaphthalene, behaved quite well also, especially when compared with $C_{12}F_{22}$ whose two rings are joined by a C—C single bond. Whereas at 100°C the perfluoronaphthalene and perfluorobicyclohexyl showed similar stability (BNL 841, p. 20), at 450°C they are many orders of magnitude apart. Apparently rings as such are not particularly sensitive to radiation, and might even be considered to confer stability.

Carbon Tetrafluoride

Reed and Mailen at the University of Florida had reported C_2F_2 and C_2F_6 as the major products of CF_4 irradiation. At Brookhaven some CF_4 was irradiated and the chromatographic fraction that was supposed to be C_2F_2 was collected. It turned out to be instead the oxide or ether, CF_3-O-CF_3 , unequivocally shown by its infrared spectrum. In this experiment no C_2F_6 or higher perfluoroalkanes were formed, and these results were shown to be due to the presence of about 1% oxygen in the CF_4 . Apparently oxygen is a good scavenger for CF_3 radicals, preventing formation of the C_2F_6 usually observed. As oxygen was removed from the starting material, C_2F_6 began to show up in the products and eventually predominated. At 350 ppm oxygen, the G -value for C_2F_6 formation was determined as 1.4×10^{-2} in a γ irradiation of $\approx 10^9$ rads at 50°C . With about 1% oxygen present, the G -value for CF_3-O-CF_3 formation was 5×10^{-2} .

These G -values are considerably lower than those obtained by others who have worked with either lower or higher CF_4 pressures, and lower doses. In order to try to resolve this discrepancy, the effect of pressure and of dose is currently being investigated. In addition, an attempt is being made to remove oxygen to a value of the order of a few ppm and to measure accurately the amount of free fluorine produced in the radiolysis. The latter is of interest since elemental F_2 has never been detected in the radiolysis of fluorocarbons, in contrast to hydrocarbons where H_2 is always a product. F_2 must be produced in the radiolysis of CF_4 , and when it can be determined quantitatively, it will be attempted to discover whether or not it is formed in radiolysis of higher fluorocarbons.

NOBLE GAS CHEMISTRY

D. MACKENZIE, J. FAJER, D. RIEL

Gas-Phase Irradiations

Cyclotron irradiations were continued in an effort to prepare KrF_4 . It is rather definitely established now [Schreiner, Malm, and Hindman, *J. Am. Chem. Soc.* **87**, 21 (1965)] that Grosse et al., in their early work purporting to have made KrF_4 , really prepared KrF_2 with perhaps traces of KrF_4 . Since the low temperature and low F_2 :Kr ratio used at Brookhaven favored KrF_2 formation, the F_2 :Kr ratio was increased to 10 and went to temperatures as high as -60°C . Infrared spectra of the products in all cases showed only KrF_2 .

Since xenon compounds of chlorine had not been reported, and none could be prepared by irradiating Cl_2 -Xe mixtures at low temperature, it was decided to see if a mixed chloride-fluoride

might be stable enough to isolate. Accordingly, a 1:1:1 mixture of F_2 , Cl_2 , and Xe was irradiated at about -25°C and a total pressure of 2 atm. A white crystalline compound was frozen out in a quartz U-tube as product was pumped from the reaction vessel. This behaved much like XeF_2 , but on warming with a hair dryer elemental chlorine was formed. Because of the apparent mixture of XeF_2 and chlorine-containing compound, the latter could not be identified.

The experiment has been repeated a number of times in an effort to isolate the chlorine-containing compound from the XeF_2 , or at least to obtain an infrared spectrum of the two compounds together. The separation has not been achieved, and no infrared peaks have been obtained that can be definitely assigned to the chlorine-containing compound. Its method of formation and behavior suggest it might be a complex of XeF_2 and ClF . It is planned to attempt synthesis of such a complex by simple chemical reaction of XeF_2 and ClF .

Theoretical work [e.g., B.-M. FUNG, *J. Phys. Chem.* **69**, 596 (1965)] suggested that other noble gas compounds might be stable. Irradiation of

Figure 6. Infrared absorption of products from irradiation of XeF_2 with liquid fluorine. XeF_2 absorbs at 550 and 566 cm^{-1} , XeF_4 at 580 and 590 cm^{-1} , XeOF_4 at 608 cm^{-1} , and XeF_6 at 612 cm^{-1} . The chart paper for this spectrum was apparently displaced a few cm^{-1} to the left.

BF₃-Ne and CO-Xe mixtures at -78°C yielded no detectable products.

An interesting gas-phase reaction requiring no irradiation is that represented by the equation $\text{KrF}_2 + \text{Xe} \rightarrow \text{Kr} + \text{XeF}_2$. It was found that this reaction proceeded spontaneously when a KrF₂:Xe mixture which had been frozen into a nickel cell was allowed to warm to room temperature. This is a good example of the strong oxidizing power of KrF₂.

Condensed Phase Irradiations

Since attempts to prepare KrF₄ in the gas phase were unsuccessful, it was decided to irradiate KrF₂ in the presence of liquid fluorine. An experiment using XeF₂ was first carried out to test the method. Since the range of 10-MeV protons in these condensed phases is of the order of 1 mm, a thin layer of XeF₂ was frozen on the inside of the cell window and the cell filled with liquid fluorine. After one hour's irradiation, the XeF₂ had almost all been converted to XeF₄ and XeF₆, as shown by the infrared spectrum of Figure 6. Several irradiations, both proton and particle, using KrF₂ in a similar way, yielded no identifiable KrF₄. An impurity with infrared absorption in the region where KrF₄ should absorb prevented a conclusion as to whether any KrF₄ had been formed, but it was obvious that the bulk of the "product" was unchanged KrF₂.

A similar technique was used with solid Xe and liquid O₂ with inconclusive results. After irradiation the excess oxygen and xenon were pumped away and dilute base was admitted to the reaction cell. A small amount of oxidizing powder was found in the aqueous solution but it was not definitely identified as perxenate ion. One other irradiation of interest was that of a liquid-phase mixture of Xe and Cl₂ at $\approx -100^\circ\text{C}$. Since apparently no compound was formed at this temperature, it seems dubious that any xenon chlorides are stable above -100°C .

It is planned to do some irradiations in the Cosmotron using protons of several hundred MeV with a range of many cm in liquids or high pressure gases. One advantage of the Cosmotron is its pulsed beam that delivers a short pulse of 10-in. protons every 2 to 3 sec. This allows time for any reaction products formed in the intense radiation burst to be removed from the beam path before the next pulse arrives. As well as trying several experiments in the noble gas field, it is planned to

apply the technique to preparation of thermally sensitive compounds (particularly higher fluorides) of the transition elements.

ENERGY STORAGE

R. WISWALL, S. JAMES, J. REILLY

The development of chemical systems suitable for the storage of cheap central-station power continues to appear desirable. Research in this field falls into two parts, on storage proper and on release. The most efficient methods of release will almost certainly be electrochemical. A program was therefore started, two years ago, on the fundamental kinetics of certain electrode processes selected for their probable relevance in energy storage and release cycles. This work was first reported in BNL 900; its continuation is described below.

During the past year, a program has also been started on storage reactions. The main emphasis is on the reversible conversion of hydrogen – the simplest chemical fuel that can be made from electricity – into metal hydrides.

Electrode Kinetics

Homogeneous Reaction $\text{O}_2 + \text{Tl(I)}$. Previous work [BNL 900 (S-67)] found no oxidation of Tl(I) by O₂ in H₂SO₄ below 80°C in the absence of a catalyst. Since the difference between the potentials of the O₂/H₂O and Tl(III)/Tl(I) couples is 0.5 volts greater in HCl than in H₂SO₄, a high rate of oxidation is more likely in HCl. The following are results obtained in HCl at 25°C. In some cases an excess of active carbon of specific surface 500 m²/g was added as catalyst.

Medium	k_2 for $\text{O}_2 + \text{Tl(I)} \rightarrow \text{Tl(III)}$
1 F HCl	$< 30 \times 10^{-5} \text{ F}^{-1} \text{ sec}^{-1}$
1 F HCl + carbon	30×10^{-3}
12 F HCl	6×10^{-3}
12 F HCl + carbon	$\approx 60 \times 10^{-3}$

These rates are disappointingly low [compare k_2 of 700 F⁻¹ sec⁻¹ for the titrimetrically useful oxidation of Fe(II) by Ce(IV)] and augur poorly for the use of Tl in catalyzing the electrolytic reduction of O₂.

Electrode Reaction $\text{Tl(I)} \rightleftharpoons \text{Tl(III)} + 2\text{e}$. Work described previously at a Pt rotating disc electrode in 5 F H₂SO₄ has been extended to varying H₂SO₄ and Tl concentrations and also to 2 F HNO₃, 1 and 10 F HClO₄, and 1 F HCl.

The experimental current (i) vs voltage (E) curves are much more complex than those found

by previous workers in essentially similar studies in H_2SO_4 and HClO_4 . The curves obtained in this work display anomalies on both anodic and cathodic sides of equilibrium E . In H_2SO_4 , HClO_4 , and HNO_3 , where $E = +1.25$ V [*vs* normal hydrogen electrode (NHE)], the cathodic wave has a well-defined prewave, maximum and minimum, before limiting cathodic i is attained at $+0.7$ V, NHE. The anodic wave sometimes exhibits an inflection before that corresponding to the limiting anodic i at $+1.8$ V, NHE. The i - E curves differ greatly according to whether anodic (from negative to positive voltages) or cathodic scanning is employed, corresponding to starting with a reduced or oxidized electrode, respectively. With cathodic scanning (a) the first anodic inflection is always absent, (b) i is much lower over the whole wave, and (c) E 's of the maximum and minimum in the cathodic wave are displaced cathodically by 0.2 V relative to those during anodic scanning. The use of Tl from three different sources, of the three different acids as supporting electrolytes, and of a careful purification procedure made no basic difference to the i - E 's recorded, thus precluding the influence of adventitious impurities.

It is probable that the peculiarities of the i - E curves are connected with the slow adjustment of the Pt surface toward equilibrium states of oxidation as its potential changes. The facts that surface oxidation of Pt ($E^0 = +1.0$ V, NHE in H_2SO_4 , HClO_4 , and HNO_3) is a slow process subject to hysteresis and that electrode reactions are generally faster at reduced than at oxidized Pt could account for (b) and (c) above. However, at a boron carbide rotating disc electrode, a cathodic prewave is observed somewhat similar to that at Pt although relatively vestigial. This complicates matters since boron carbide is reputedly inert to oxidation.

Tl(I) and Tl(III) are known to suffer specific physical adsorption at Pt and the potential-dependence of this process might account for the observed anomalies. However, the great rapidity of physical adsorption cannot be reconciled with the pronounced hysteresis obtained in i - E curves. Similar considerations apply to double-layer effects which should be established almost instantaneously. Of course adsorption and double-layer effects might cooperate with surface oxidation in producing the observed curves.

The study of thallium is being wound up with i - E 's in HCl solution where radical differences might be expected since (a) Tl tends to exist as complex anions in HCl and (b) in HCl the Tl(III-I) potential is very close to that for Pt oxidation.

Hydride Formation

A survey of the known metal hydrides shows that almost all which can be formed by direct union of the elements have decomposition temperatures (where $P_{\text{H}_2} = 1$ atm) of 275°C or higher. (An exception is palladium, but its cost rules it out as a hydrogen "tank.") The heat that must be supplied to a hydride in order to recover hydrogen from it represents an inefficiency in the energy-storage cycle; and the higher grade the heat, the worse the inefficiency. The ideal hydride for storage purposes would decompose at the temperature of the device in which the product hydrogen was used. In the case of aqueous fuel cells, this would be 150° , or at most 200°C .

The decomposition temperature of a metal hydride can sometimes be lowered by mixing it with a metal which can form an exothermic alloy or intermetallic compound with the metal of the hydride; an example is the effect of aluminum on lithium hydride (The solid state reaction of lithium hydride and aluminum. S. ARONSON and F. J. SALZANO, Informal Report BNL 9230). Exploitation of this effect may permit the development of hydrogen-storage systems more amenable to practical use than any now known. The available information on the thermodynamic properties of the alloys of hydride-forming metals has been examined, and a number of promising systems has turned up. For a start experiments were begun on the system Ni-Mg- H_2 .

Preliminary data obtained with the Ni-Mg- H_2 system are listed in Table 5. These data are equilibrium decomposition pressures and are shown

Table 5

Equilibrium Pressure (psia)

Temperature, $^\circ\text{C}$	Ni-Mg- H_2 (solid)	Mg H_2 (extrapolated) ^a
186	0.1	0.05
221	4.3	2.2
246	11.0	5.4
268	20.2	10.3

^aJ. Am. Chem. Soc. 82, 3504 (1960).

compared with extrapolated values for MgH_2 . Not only are the pressures of Ni-Mg- H_2 systems higher by a factor of 2, but the rate of attainment of equilibrium was greatly increased and the pressures shown were recorded one-half hour after reaching the corresponding temperature. By contrast, the values for MgH_2 were extrapolated from high temperature-high pressure values reported in the literature because the decomposition at the temperature shown is very slow and equilibrium, for all practical purposes, cannot be attained.

A somewhat different approach to the use of hydrides as energy storage media lies in the direct cathodic formation of the hydride. Several metals, such as zirconium and thorium, have been observed to form superficial hydride films when made cathodes in aqueous electrolytes. An experimental study of this and related effects is planned.

MECHANISM OF GRAPHITE FORMATION

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High Temperature Studies

In studying the mechanism of graphite formation from a hydrogen-hydrocarbon system, the

mechanism of the reaction of H_2 and graphite and the gaseous species above the graphite are being investigated.

The reaction of H_2 with graphite is almost entirely a surface reaction below 2700°K , but above this temperature the vaporization of graphite to C_n species becomes significant and the reaction of these with gaseous hydrogen is the principal reaction above 3200°K . The final product from the low temperature reaction is CH_4 with small amounts of C_2H_6 at the higher pressures and temperatures. Above 3200°K the final product is acetylene with small amounts of C_3H_8 at short reaction times.

In previous work the reaction rate was determined using a graphite filament heated by alternating current. At high energy inputs the temperature of the filament fluctuated 150°C , 120 times per second. This was shown experimentally when a photoelectric pyrometer having a 1-msec response time was displayed on a double trace oscilloscope. The other trace was used to determine the current and thus the watts at short reaction times. To eliminate this temperature fluctuation, the present results were obtained using a 120-V storage-battery power source capable of operating at 200 A.

Using this apparatus the reaction of graphite and H_2 was studied from 0.01 to 1.0-atm pressure and 2000° to 2900°K . The rate of reaction was determined by analyzing the hydrocarbon product with a vapor-phase chromatographic apparatus. In carrying out these runs the length of time was adjusted so that $<5\%$ of the filament reacted and also so that the final C/H ratio was $<20\%$ of the equilibrium value.

The results for runs in which the time was >2 sec (and thus the temperature could be read by an optical pyrometer) are summarized in Figure 7. For the results above 2631°K the vaporization of graphite becomes significant, so that only temperatures below this were considered in determining the rate of the surface reaction. The rate for this region can be given by the equation

Rate of reaction

$$= 80P(\text{H}_2) \sqrt{K_D} = 80P(\text{H}) \sqrt{P(\text{H}_2)}, \quad (1)$$

where the rate is given in $\mu\text{moles/sec}$, the hydrogen pressure $[P(\text{H}_2)]$, the atomic hydrogen pressure $[P(\text{H})]$, and the dissociation constant of hydrogen (K_D) are given in atmospheres.

Figure 7. Reaction of graphite and hydrogen.

The calculated values agree with the experimental values within a factor of two for pressure range of 10^2 and a rate change of 10^3 . The experimental results agree with the calculated values within experimental error except for the results at 76 mm which appear significantly lower. It was recently found that the specific surface area of different filaments varied by a factor of two and may account for some of the variation. A theoretical explanation of equation (1) would involve adsorption of molecular H_2 on particular sites of graphite proportional to $\sqrt{P(H_2)}$ followed by collision with atomic hydrogen to form methyl radicals. Methyl radicals would yield methane in the gas phase and only at high reaction rates would they become sufficiently concentrated to form ethane by bimolecular collision. No acetylene was formed below $2600^\circ K$.

The rate of evaporation of graphite is also shown in Figure 7 and was found to be the same in the presence of N_2 , He, or CH_4 as in a vacuum. At 7.6 mm and at temperatures above $2600^\circ K$, the rate of reaction is less than the rate of vaporization of graphite. At this pressure vaporized carbon species appear to polymerize and cool rather than react with H_2 . Thus there is a greater weight loss of filament than hydrocarbon product formed.

Surface Area Studies

In earlier work it was shown that with nuclear graphite (TSX) the roughness factor R (the increase in specific surface area per incremental increase in specific geometrical surface area) had a value of 50 and could be accounted for by the opening of closed pores. R was found to remain constant for sieved graphite samples for particles between 77 and $1000\ \mu$ in diameter. When the external dimension of a particle approaches the length of the closed pores, the value of R should decrease and reach a value of 1 when all the pores are open. Since standard sieve openings are too large and small graphite particles stick together when dispersed in a gas, 140 to 170-mesh TSX graphite was further subdivided by grinding it in a ball mill using $\frac{1}{16}$ -in. nylon beads. The specific surface area of the pulverized graphite increased linearly with time of grinding until it reached $15\ m^2/g$ and then increased at a continually decreasing rate to $37\ m^2/g$. Assuming that the specific geometrical surface area increases linearly with grinding time, it is estimated that the total surface

area of the closed pores is $30\ m^2/g$ or $50\ m^2/cm^3$. From the helium density measurements of pulverized TSX, the volume fraction of the closed pores is estimated to be 0.01. Our experimental results are consistent with the following picture of the closed pores: pores have an average depth of $15\ \text{\AA}$, a width of $45\ \text{\AA}$, and a length of $15\ \mu$. The number of closed pores would have to be $10^{14}/cm^3$ to obtain $50\ m^2/cm^3$. Pore size determinations using N_2 adsorption show that most of the surface area of pulverized TSX is accounted for by pores of $< 20\ \text{\AA}$ diam (when calculated as cylindrical pores). Since it would be expected that the pores are not uniform, some of the pores must have a depth of $10\ \text{\AA}$ or less to make up for other pores having depths of $20\ \text{\AA}$.

Chemical Technology

FLUORIDE VOLATILITY PROCESS

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The nitrofluor process for treating reactor fuel is based on fuel dissolution in anhydrous HF solutions containing N_2O_4 , N_2O_3 , or NOF as complexing agents. These solutions are capable of dissolving a variety of fuels because of the reactivity of the nitrosyl ion (NO^+). After dissolution of the fuel, the liquid phase is evaporated and the solid residue is selectively fluorinated in order to separately volatilize U and Pu from the fission products and structural materials. Final purification of the U and Pu can be performed by one or more methods already established. The work this year consisted of investigating the dissolution of kilogram amounts of fuel in the $95^\circ C$ azeotrope ($NOF \cdot 3.1HF \cdot <0.1\ N_2O_3$); related process studies were conducted on a smaller scale.

Engineering-Scale Experiments

U-Zr Alloy Fuel Dissolution. A full cross-sectional portion of this enriched fuel was dissolved in the $95^\circ C$ azeotrope using the Monel dissolver and associated equipment. The 6-in. pipe dissolver contained an internal helical coil and was surmounted on the salt receiver vessel into which precipitated material settled. The working volume of this combination was ≈ 21 gal. Anhydrous HF was pumped through the coil and an external heat

exchanger which was either cooled or heated with water. The fuel was suspended inside the coil, near its lower end, using Monel wire fastened to the dissolver head flange. A wire mesh screen retained detached fragments of fuel until they dissolved. Off-gas from the dissolver was manually vented to the gas receiver and the rate of pressure rise was used to determine the dissolution rates.

The 7.84-kg piece of Zircaloy-uranium fuel reacted with the solvent at room temperature. With cold HF flowing through the coil, the temperature of the solution above the fuel increased to 120°C in 5 min. The average dissolution rate for this period was 227 g Zr/min. The NO gas evolved was vented continuously at 70 psig. In accordance with previous experience, the reaction rate subsequently decreased and intermittent cooling and venting was used thereafter. Three additions of solvent were made to maintain the liquid level, and nitrogen sparging of the salt receiver increased the dissolution rate to a maximum of 409 g Zr/min in the solution temperature range 100° to 130°C. The fuel dissolved in 2¼ hr, as determined by a rapid decrease in temperature and the end of NO evolution. Of the 25 gal of azeotrope added to the system, 16.5 gal was recovered in the batch evaporator after the venting of free HF. There was no visible sign of corrosion inside the dissolver.

UO₂ Fuel Rod Dissolution. A 9-rod array simulating a portion of Yankee reactor fuel was dissolved in 20 gal of the 95°C azeotrope. The 3-ft-long assembly contained 3.1 kg UO₂ and 1.1 kg

SS. External electric heating was used on the dissolver and dissolution of the cladding began at a solution temperature of 82°C. The venting of NO gas was started at 104°C when the dissolving rate increased markedly. After 2 hr, the cladding was half dissolved and NO₂ from the reaction with UO₂ was observed. The solution was sparged twice and maintained at 110° to 116°C for the next 2 hr. During the 4 hr of dissolution, all the UO₂ and cladding dissolved; the remaining 18% of the stainless steel and brazing compound are shown in Figure 8.

U-Al Alloy Fuel Dissolution. A full-size assembly of fuel, weighing 5.2 kg and containing 151 g enriched U, was almost completely dissolved in about 30 gal of the 95°C azeotrope which was heated to 116° to 127°C for 12 hr. Upon heating of the solution, NO evolution began when the temperature reached 50°C; it was vented at pressures as high as 110 psig. Additional solvent was added twice, and alternate heating and cooling were used to control the temperature. The separated condition of the assembly after 5.5 hr of dissolution is shown in Figure 9; the fuel alloy area of the plates was exposed and 67% of the assembly had dissolved. The dissolution was continued for 6.5 hr, after which only 186 g Al remained. By employing a higher solvent:fuel ratio, the assembly could have been dissolved in less time.

In future work a cylindrical nickel dissolver will be used, and after evaporation of the solvent, UF₆ will be volatilized from the salt residue by

Figure 8. Stainless steel fuel remaining after dissolution of UO₂-SS fuel assembly.

treating it with BrF_3 at 150°C . The dissolver and associated equipment for U recovery experiments are being installed in the equipment enclosure, and testing is scheduled to begin early in 1966.

Separation Studies

High-Enrichment Fuels. The separation of U from dissolved fuels was studied on a small scale using BrF_3 to volatilize UF_6 from the complex salt mixture remaining in the dissolver after evaporation of the solvent. For a Zr alloy fuel containing 5 g U, a series of 5 BrF_3 treatments at 135° to 150°C removed 99.4% U. Each treatment lasted several hours, and 1.35 liters of BrF_3 were used. In experiments during which the BrF_3 was replenished after small fractions were vaporized through a reflux condenser, more efficient use of the BrF_3 was made but 2.5% of the U was not volatilized. Increased contact, by mixing for example, is expected to improve the separation of U.

Similar experiments on the separation of U from dissolved U-Al alloy fuel were tried with 1 to 2 g of fuel plate or an equivalent amount of the metals. It was shown that extensive drying reduced UF_6 volatilization and that with damp salt only 0.3% of the U was retained after four 15-min treatments at 150°C using a total of 70 ml BrF_3 . Under reflux conditions, with the BrF_3 at 160° to 177°C , the same result was obtained with a total of 35 ml BrF_3 used in two treatments. With improved control of the reflux condenser, the U loss was reduced to 0.15% with 40 ml BrF_3 .

Low-Enrichment Fuels. Relatively few experiments have been performed on the removal of U and Pu from salt mixtures prepared in a dissolver. The U can be separately volatilized as NOUF_6 or UF_6 by more than one method; however, PuF_6 can be volatilized only by contacting the salt mixture with F_2 gas at elevated temperatures.

In an experiment utilizing the dissolution products of 5.5 g UO_2 , 193 mg of the oxides of fission product elements, and 122 mg Pu metal, 99.6% U was volatilized as NOUF_6 during heating in a nickel tube at 420°C . More than half of the NOUF_6 transferred with simple heating, and the remainder was volatilized by vapor from the 95°C azeotrope. About 3% Pu was entrained with the NOUF_6 . Subsequent treatment with a stream of F_2 at 500°C for 2 hr volatilized all but 3.9% of the Pu. In related experiments it was previously shown that longer fluorination will remove practically all

Figure 9. U-Al alloy fuel assembly after 5.5-hr dissolution in the 95°C azeotrope.

the Pu. The pink Pu compound, which has been tentatively identified as NOPuF_5 , decomposes to PuF_4 and nitrogen oxides when heated.

The behavior of heated NOUF_6 , as observed in a quartz apparatus, consisted of some initial gas evolution followed by a change in color to bright green, and subsequent vaporization of the dark liquid at 300°C . The condensed material exhibited the same behavior, and in each case a small amount of UF_4 and UO_2F_2 remained behind.

A new method of volatilizing UF_6 from a dissolver solution of the 95°C azeotrope is based on the action of excess HF on NOUF_6 . The NOF removed by the HF leaves UF_5 which can be converted to UF_6 by the addition of F_2 . With simple systems of NOUF_6 and HF, or $\text{NOUF}_6 + 95^\circ\text{C}$ azeotrope + excess HF, an apparently slow reaction with gaseous F_2 at room temperature yielded a solution from which 93 to 99% of the U was volatilized as UF_6 at room temperature. In scouting experiments with partially spent dissolver solutions of three fuels (U-Zr, U-Al, and UO_2 -SS), F_2 treatment at room temperature permitted about 90% of the U to be volatilized at 110°C .

Corrosion Studies

In preparation of the 95°C azeotrope from NOCl and HF, a considerable portion of the

yield consists of the azeotrope $\text{N}_2\text{O}_3 \cdot 12.6\text{HF}$ boiling at 68°C . Although this material is a good dissolving agent, it has caused corrosion in Monel equipment. Fundamental corrosion studies with this solvent were made using electrical resistance measurement as a method of following small dimensional changes in wire probes exposed to the environment. Construction of the probes was simplified, and minor modifications of the previously described apparatus improved the temperature stability and the precision of measurement. The corrosion of Monel alloy 400 and Nickel 200 was studied in redistilled 68°C azeotrope as a function of time and temperature in the elastic and plastic ranges. In the case of Monel, a protective film formed after 0.01 to 0.02-mil corrosion at temperatures exceeding $\approx 100^\circ\text{C}$. Temperature cycling from 150° to 0°C occasionally caused temporary disruption of the protective film. The corrosion of nickel was substantially less than that of Monel, and the protective film formed more rapidly. The film was also more adherent and less affected by temperature cycling. Protective film formation was not significantly affected by stressing these metals.

Tests with 68°C azeotrope containing dissolved UO_2 (NOUF_6), and presumably water formed in this reaction, showed that there was no measurable corrosion of nickel after the short initial period required to obtain temperature equilibrium. The protective film seemed stable when load and temperature changes were made. With Monel, ≈ 0.1 mil of corrosion occurred over a period of several hours before a semiprotective film formed. Thereafter slow corrosion continued for several days at a rate of 0.001 mil/hr (0.7 mil/mo). The effect of load and temperature cycling was not determined. Thus nickel is superior to Monel for both applications.

VOLATILITY FUEL PROCESSING

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The pilot plant used in the reprocessing of un-irradiated Rover (graphite) fuel was modified for use with stainless steel-clad and Zircaloy-2-clad UO_2 fuels. In addition, experiments were carried out in the oxidation unit of the plant with graphite matrix fuels containing both uranium and thorium, i.e., High Temperature Gas-Cooled Reactor (HTGR) fuel.

Figure 10. Pilot plant flow diagram for clad fuel reprocessing.

Figure 11. Pilot plant fluidized bed reactor

Clad UO_2 Fuels – Pilot Plant Work

Figure 10 shows a simplified flow diagram of the equipment used in the studies with clad UO_2 fuels. The two-step process is essentially the same for both stainless steel and Zircaloy-clad fuels. The fuel assembly, immersed in a fluidized bed of granular alumina, is contacted with a mixture of HF and O_2 at $\approx 600^\circ\text{C}$. This produces a rapid disintegration of the cladding by fluoride-promoted oxidation and exposes the U (and/or Pu) for subsequent reaction with F_2 and recovery as the volatile hexafluoride.

Figure 11 is a diagram of the 4-in.-diam reaction vessel in which both the decladding and

Figure 12. Yankee type fuel assembly (16-rod, 15-in.- long) charged to Run 3, 2.5 kg UO_2 - 0.8 kg stainless steel.

Figure 13. Zircaloy-2 clad UO_2 fuel assembly (9-rod, 30-in.-long) charged to Run 4, 3.4 kg UO_2 - 0.9 kg Zircaloy-2.

Table 6

Pilot Plant Run Summary

Run	Yankee fuel			Zircaloy-2 fuel
	SS-1	SS-2	SS-3	Zr-1
Fuel	9-rod, 15-in. long	9-rod, 30-in. long	16-rod, 15-in. long	9-rod, 30-in. long
UO_2 content, kg	1.410	2.930	2.509	3.357
Total stainless steel or Zircaloy-2 content, kg	0.440	0.838	0.792	0.916
Total weight of fuel, kg	1.850	3.768	3.301	4.273
Alumina charge, kg	18.2	23.6	18.2	23.6
U/ Al_2O_3 ratio	0.068	0.110	0.121	0.125
Cladding/ Al_2O_3 ratio ^a	0.044	0.064	0.079	0.062
HF-oxidation				
40% HF-60% O_2	39 min	1 hr	1 hr, 15 min	30 min
25% HF-75% O_2	1 hr, 51 min	3 hr, 20 min	3 hr, 28 min	2 hr, 30 min
Total	2 hr, 30 min	4 hr, 20 min	4 hr, 43 min	3 hr
Fluorination				
25% F_2 -75% N_2		2 hr, 20 min	2 hr, 20 min	2 hr, 28 min
50% F_2 -50% N_2		1 hr, 5 min	1 hr, 0 min	30 min
Total time	2 hr, 20 min	3 hr, 25 min	3 hr, 20 min	2 hr, 58 min
Total F_2 charge, lb	6	10	10	7.5
U in bed after fluorination, %	0.025	0.107	0.16	0.17

^a Assumed: 30% Cr volatilized, remainder as Cr_2O_3 , Fe as FeF_3 , and Ni as NiF_2 . Zr-2 clad residue assumed to be 50% ZrO_2 -50% ZrF_4 .

the fluorination steps are carried out. Four runs have been made with small assemblies of clad fuel rods made up with the same spacing used in actual fuel assemblies. In three of these runs sections of Yankee reactor type fuel, stainless steel-clad UO_2 (Figure 12), were used; in the fourth run the rods were Zircaloy tubing filled with UO_2 pellets (Figure 13). The fuel assemblies were reacted with the optimum 40% HF -60% O_2 mixture, at a 0.75-ft/sec superficial velocity. As the UO_2 pellets became exposed to the gases, the HF concentration was lowered to $\approx 25\%$ to promote breakup of UO_2 to fine U_3O_8 , and to minimize the formation of UO_2F_2 . This two-step procedure is based on bench-scale tests reported below. Table 6 shows the results obtained in both the decladding and fluorination steps. Temperature control during all decladding runs was good.

The fluorination step was initiated at a bed temperature of 450°F with a 25% F_2 -75% N_2 mixture at a superficial velocity of 0.6 to 0.75 ft/sec. Temperature and F_2 concentration were increased during the runs to 525°C and 50%, respectively. The reactions were smooth with no indications of temperature excursion or bed caking. The runs were terminated after 2 to $3\frac{1}{2}$ hr of fluorination. Residual uranium concentration in the bed was 0.025 to 0.17 wt %.

Clad UO_2 Fuels - Bench-Scale Work

As indicated previously, the reaction of HF-O_2 with exposed UO_2 in the decladding of stainless

steel-clad fuel rods may result in the formation of UO_2F_2 as well as U_3O_8 . The UO_2F_2 tends to form as large pieces which are not suitable for reaction with F_2 . In order to prevent excessive heat generation and bed caking during the fluorination, substantial breakup and dispersion of the UO_2 reaction product is required.

Experiments were carried out, therefore, to determine optimum decladding conditions to promote the formation of U_3O_8 rather than UO_2F_2 , without seriously reducing the rate of attack on the stainless steel. Sintered UO_2 pellets (0.3 in. diam by 0.6 in. long) were exposed to HF-O_2 mixtures at 600°C in a boat and the reaction product was screened to determine particle size distribution. The results, presented in Table 7, show that a finely divided U_3O_8 product was obtained at the lowest IIF concentration used (20% HF -80% O_2), and that the average particle size increased to a coarse UO_2F_2 product with the higher HF concentrations. At 650°C , satisfactory UO_2 particle size reduction was obtained with the 20% HF -80% O_2 . A high rate of attack on the stainless steel was also obtained with these conditions, i.e., 40 mils/hr.

A second approach was to carry out the decladding step under conditions of maximum penetration, i.e., with 40% HF , 60% O_2 , and 650°C , then reduce the coarse UO_2F_2 - U_3O_8 product with H_2 to give UO_2 and, finally, reoxidize with O_2 to U_3O_8 . Several pellets of sintered UO_2 were exposed to 40% HF -60% O_2 at 650°C to form a coarse UO_2F_2 - U_3O_8 product which was then re-

Table 7

Particle Size Distribution of Single UO_2 Pellet Reaction Product After Exposure to HF-O_2 Mixtures

U.S. mesh size	Wt % of product			
	20% HF -80% O_2 at 650°C for $1\frac{1}{2}$ hr	20% HF -80% O_2 at 600°C for 2 hr	30% HF -70% O_2 at 600°C for $1\frac{1}{2}$ hr	40% HF -60% O_2 at 600°C for $1\frac{1}{2}$ hr
+8	10	1.2	13	33
+8-16	2.3	0.3	2.3	12
+16-40	6.2	1.7	7.4	14
+40-60	6.4	2.8	6.7	7.0
+60-120	15	12	13	10
+120-200	20	27	26	10
-200	31	43	21	6.3
Recovery ^a	91	88	89	92
Estimated stainless steel penetration rate, mils/hr	42	2	16	31

^aWith the small quantities involved, low recovery is believed to be due mainly to loss of fines.

Figure 14. Left: HTGR fuel compact; right: broken HTGR fuel compact, typical of material charged to oxidizer.

acted with 100% H_2 for 30 min at $650^\circ C$ and, after purging with N_2 , further reacted with O_2 at $400^\circ C$. The resultant product was fine U_3O_8 . These boat experiments were followed by fluid-bed runs in which a 3-in.-deep bed of products from the reaction of Yankee type fuel and a 45% HF -55% O_2 mixture was treated with a 50% H_2 -50% N_2 mixture at $625^\circ C$ for 1 hr. The bed was then reacted with 50% O_2 -50% N_2 at $400^\circ C$ and the fine U_3O_8 particles were produced with no evidence of coarse UO_2F_2 remaining.

Clad UO_2 Fuels – Other Studies

Other studies were carried out on the following.

- (1) The effect of buildup of stainless steel de-cladding products in the fluidized bed on caking and fluidization quality during recycle operation.
- (2) Elutriation of fine fluorides from the bed as a means of extending bed life.
- (3) Volatilization of $FeCl_3$ from the fluidized bed with CCl_4 as a means of extending bed life.
- (4) Volatilization of chromium compounds, mainly CrO_2F_2 , during fluorination.

HTGR Fuels

The fuel used in the work described below was the type "A" compact (Figure 14) obtained from the General Atomics Co. and which has a nominal composition of 3% U, 15% Th, and 82% C.

In the oxidation step the major reactions are

In the fluorination step the principle reaction is

Oxidation Step. At the beginning of a run the oxidizer (Figure 15) was filled to a depth of ≈ 3 ft with 16 kg of refractory, granular alumina. The HTGR compacts were charged into the oxidizer in the form of pieces $\approx 1 \times \frac{3}{4} \times \frac{3}{4}$ in. The initial charge of fuel was 830 g after which fuel was added periodically in 1-kg increments (Figure 16) for a total charge of 11.190 kg. After the start-up period, the oxygen feed rate was maintained at 1.4 to 1.5 SCFM and the bed center line temperature was held at $740^\circ C$ while cooling air was circulated in the annular space to hold wall temperatures to a maximum of $735^\circ C$. Graphite fuel was added as required to keep the O_2 utilization (i.e., the burning rate) high. Bed material was not drawn off continually because an insufficient supply of fuel was not available to sustain continuous operation.

Figure 16 shows a plot of (1) off-gas composition, (2) temperature at the middle of the fluidized bed, and (3) weight of fuel charged to the reactor *vs* time (for the entire oxidation run). The cumulative quantity of the product oxides expressed as

Figure 15. Pilot plant fluidized bed oxidizer.

grams of uranium and thorium is also shown. Higher O_2 utilization could have been attained by operating at a higher temperature ($\approx 800^\circ C$); however, because of strength limitations the nickel reactor wall temperature was held below $735^\circ C$.

After the last fuel addition, the oxidation was continued for ≈ 8 hr at which point the off-gas contained $<0.1\%$ C (as CO_2 or CO). The reactor was then cooled and the bed drained. The bed was found to be free flowing and was easily removed through the drain line. By analysis, the bed material contained 2.35 wt % U_3O_8 and 8.9 wt % ThO_2 . The oxidation proceeded smoothly and no difficulties were encountered with temperature or reaction control.

Fluorination Step. Because modifications were being made in the fluorinator unit of the pilot plant, the uranium recovery step was carried out in a 2-in. unit (Figure 17).

The procedure was similar to that described above for UO_2 fuel with the following exceptions.

- The maximum volume percent fluorine in the fluidizing gas was increased from 50 to 100%.
- The fluorination temperature was increased to $550^\circ C$ over the course of the reaction.

Figure 16. Oxidation of HTGR fuel.

(c) An intermediate pyrohydrolysis step was required to obtain satisfactory uranium recovery.

(d) The fluidizing gas feed rate during fluorination was 0.33 SCFM.

The results of a number of fluorination experiments are shown in Table 8. In an effort to improve the over-all recovery, the beds used in experiments HF2 and HF4 were recycled. However, in both cases the fluidization of the bed in the second cycle (HF3 and HF5) was poor because of bed caking, and the uranium recovery was low. The deterioration of fluidization quality was attributed to the amount of ThF_4 in the bed which built up to $\approx 40\%$ of the bed weight. Satisfactory uranium re-

covery was obtained only with an intermediate pyrohydrolysis step as in experiments HF6 and HF7.

Figure 18 shows uranium concentration *vs* fluorination time for experiments HF6 and illustrates the effect of the pyrohydrolysis reaction.

Figure 17. HTGR bench-scale fluorination equipment.

Figure 18. Recovery of uranium from HTGR fuel oxidation products.

Table 8

Recovery of U From HTGR Fuel Oxidation Products
(Fluidized bed fluorination at 500° to 550°C.)

	Experiment No.						
	HF 1	HF 2	HF 3	HF 4	HF 5	HF 6	HF 7
Bed weight, g	1409	1500	1835	1547	1242	1455	3000
Initial U concentration in bed, weight %	2.59	2.90	2.92	4.05	4.17	2.00	2.00
Th concentration in bed, weight %	15.2	13.0	29.7	21.7	32.0	8.04	8.04
Final U concentration, weight %	0.04	0.230	0.500	0.176	0.900	0.010	0.022
% U volatilized	98.5	92.3	82.2	95.7	78.0	99.5	98.9
Total fluorination time, min	228	145	149	284	467	500	379
Bed recycled from preceding experiment	—	—	X	—	X	—	—
Pyrohydrolysis	—	—	—	—	—	X	X
Remarks		^a			^b		

^aBed caking.

^bSevere bed caking.

ULTIMATE WASTE DISPOSAL

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Phosphate Glass Process

This process involves the incorporation of high level radioactive waste into a stable phosphate glass suitable for long-term storage. Raw waste is mixed with phosphoric acid to prepare a feed solution which is first reduced in volume by evaporation at 140° to 160°C, and subsequently converted to glass by heating to 1200°C in a platinum crucible. The pilot plant, described in the previous report, for testing the phosphate glass process on a more extensive scale continued operation throughout the year. Information obtained from operation of this pilot plant formed the basis upon which PNL¹ and BNL engineers designed a prototype which will demonstrate the process with full level waste. This prototype will be installed in the Hanford Fuel Recycle Pilot Plant scheduled for operation in 1966. A full-scale copy of the prototype evaporator is being tested at Brookhaven to determine its over-all performance characteristics and observe any tendency toward scale formation on the heating surface. Laboratory efforts in the last year involved phosphate glass formation studies with wastes generated from revised fuel reprocessing flowsheets and higher uranium burnups. A technical manual describing the phosphate glass process technology was prepared for use in operating the Hanford prototype. An experimental program has been initiated to examine methods of disposal of wastes from volatility reprocessing of fuels.

Pilot Plant. The pilot plant, partially dismantled for inspection, maintenance, and modification as described in the last progress report, was reconstructed and operated intermittently throughout the year. In a series of runs the oper-

ating temperature of the evaporator was varied over the range 130° to 160°C. Based on separation of off-gas components and smoothness of over-all operation of the plant, 160°C was found to be optimum. A glass forming capacity of the plant was established as 1.3 ft³ of glass per 24 hr. At this glass production rate the evaporator, not the melter, was limiting the over-all throughput.

A number of experiments is in progress to test receiver vessels and materials of construction for suitability of long-term storage of the wastes. Thin-walled inner containers for the glass and heavy walled outer container to provide protection in transport appears feasible. Scouting tests were made on a number of materials of construction in which 2-in.-diam, 7-in.-long, closed end tubes were lilled with glass and mounted in furnaces maintained at 400°C for one month. Although both stainless and carbon steels deteriorated slightly, they will be included in further studies involving the use of inert atmospheres to minimize oxidation, controlled rates of cooling, protective coatings, etc.

Because of the corrosiveness of the melter off-gasses which contain HNO₃ and H₂SO₄, selection of a suitable construction material for a condenser was a problem. Early bench-scale experiments indicated that a cold wetted Nionel surface would resist corrosive attack. A 4-ft-long Nionel condenser with a surface area of 7 ft² was installed in the pilot plant for study. No significant corrosion was evident when the condenser was dismantled after 68 hr of plant operation. Indications are that Nionel will be a suitable material of construction; however, the test is being continued.

A review of the performance of the pilot plant and its various units was made and the results are shown in Tables 9 and 10. Of interest is the service which the Carpenter 20 evaporator has given without any appreciable signs of corrosion. In view of the absence of information concerning the strength of platinum at elevated temperature, upon which design calculations could be based, the performance of Melter No. 2, which is operated without any lateral support, is being carefully watched in periodic inspections. No significant dimensional changes or corrosion has been observed. From experience to date, it appears that platinum is suitable for long-term service in the phosphate glass processing of waste.

Waste Solidification Engineering Prototype (WSEP) Evaporator. A new evaporator, designed

¹Pacific Northwest Laboratories (operated by Battelle-Northwest at Richland, Washington).

Table 9

BNL Pilot Plant Performance Record

Operating time, yr	2
Glass formed, ft ³	43.5
Purex waste processed, gal	4500
Waste equivalent uranium, tons	57

Table 10
Equipment Service Record of BNL Phosphate Glass Plant

	Feed tank	Feed pump	Evaporator-denitrator		
			Electric	Steam	
Materials of construction	304 SS	316 SS Teflon	Carpenter 20	Carpenter 20	
Conditions					
Temperature, °C	75	75	115 to 160	115 to 160	
Pressure, cm of H ₂ O	−2		−5	−5	
Chemical	Purex + phosphate	Purex + phosphate	Purex + phosphate (concentrated and denitrated)		
Hours of use	27,046	2216	12,240	10,546	
	Evaporator, condenser, and receiver	Melter No. 1	Melter No. 2	Melter off-gas condenser	Melter off-gas condenser receiver
Materials of construction	Glass 304 SS	Platinum Inconel 702	Platinum	Nionel	304 SS
Conditions					
Temperature, °C	25	800 to 1250	800 to 1250	37	25
Pressure, cm of H ₂ O	−5			−5	−5
Chemical	HNO ₃			H ₂ SO ₄ H ₂ O (H ₃ PO ₄)	H ₂ SO ₄ H ₂ O (H ₃ PO ₄)
Hours of use	27,046	5800 ^a 1375 ^b	8454 ^a 1192 ^b	196	27,046
	Total	7175	9646		

^aBetween 800° and 1250°C.

^bUnder glass forming conditions.

Table 11
BNL-WSEP Evaporator Performance Data at 150°C^a

Run ^b	Feed rate, liters/hr	Product rate, liters/hr	Volume reduction factor	HNO ₃ /feed, vol %	Residence time, ^c hr	Specific gravity	Liquid level, ^d in.	Evaluation time, ^e hr	Total time at 150°C, hr
E-8	30.0	2.42	12.4	91.7	21.9	1.97	2.3	2.0	7.0
E-9	22.9	2.00	11.5	91.1	26.2	1.99	2.1	4.0	13.8
E-10	20.9	1.58	13.2	93.9	33.2	2.01	2.1	3.5	20.4
E-11	17.5	1.44	12.2	93.2	35.7	2.03	1.9	4.5	26.8
E-12	15.3	1.27	12.0	92.0	40.8	2.05	2.0	9.0	38.3
E-13	14.5	1.29	11.2	92.7	40.2	2.05	2.0	3.0	44.6
E-14	18.5	1.53	12.1	92.3	33.6	2.07	1.9	4.0	50.9
E-15	17.5	1.47	11.9	92.7	35.1	2.07	1.9	5.0	57.5
E-16	17.3	1.73	10.0	92.7	29.8	2.07	1.9	4.5	63.2
E-17	19.2	1.86	10.3	91.3	27.6	2.06	1.9	4.5	69.8
E-18	19.3	1.89	10.2	91.1	27.2	2.07	1.9	4.5	76.2
E-19	18.5	1.72	10.8	91.0	29.9	2.07	1.9	4.5	83.0
E-20 ^f	17.8	1.58	11.2	90.1	32.5	2.05	1.9	3.0	89.4

^aFor 80 gal/ton Purex design-basis feed (10⁴ MWD/ton); tube bundle at 173.4°C.

^bJacket steam also used in Runs E-14 through E-20.

^cSolution volume/product rate.

^dAbove top of tube bundle while boiling.

^ePeriod of evaluation (stable operation).

^f72% of Ce used in this batch of feed (short supply).

by PNL, has been under test at BNL for the last 6 months. The unit is full scale as shown in Figure 19 and is made of stainless steel whereas the prototype unit will be made of titanium. Although the unit is of a shell-and-tube type commonly used in industrial practice, its internal geometry is such that thorough testing was essential prior to use. Scaling and erosion were the most likely difficulties anticipated.

The evaporator body is 5 ft tall, its working volume is 51 to 52 liters, and the tube bundle area is 11 ft². The unit is equipped with a turbine agitator to improve circulation during operation and minimize settling under nonboiling conditions.

Some modifications to the original design, such as addition of baffles to improve the flow pattern, were made in accordance with the results of tests with the 1/10 scale glass model shown in Figure 20.

The evaporator was operated successfully with 80 gal/ton Purex design-basis feed (10⁴ MwD/ton of U) in a series of 20 runs totaling 134 hr. During the first 7 runs, the performance of the evaporator decreased so that the feed rate was reduced from

31.0 to 21.7 liters/hr with evaporator temperatures between 146° and 151°C. The progressive decrease in heat exchange capacity was attributed to a buildup of deposit on the tube surface. After the internal assembly was cleaned, some evidence of corrosion was noted on the inside of the tubes and on the draft tube at the liquid-vapor interface. The experience obtained in these initial runs was used to maintain closer operational control during the remaining runs. The results of the last 13 runs, shown in Table 11, reveal that there was a drop-off in capacity. It is believed that this is the result of operation with too high ΔT across the tubes and additional tests are planned with a revised heating program.

Volatility Waste Disposal. In considering the application of the fluid bed volatility method for reprocessing spent reactor fuels, it has become clear that effective measures must be developed for the safe and economic disposal of the wastes generated in such processes. The significant waste

Figure 19. Waste solidification engineering prototype (WSEP) evaporator.

Figure 20. Glass model evaporator used in flow studies.

arising from such processes consists of the inert aluminum oxide beds and the sodium fluoride volatile fission absorption traps which account for 99% of the total fission product activity.

Two methods of treatment of the aluminum oxide bed containing the nonvolatile fission products were proposed for early consideration: (1) leaching of the bed followed by fixation of the extracted fission products into a stable solid medium, or (2) encapsulation of the beds in low melting materials (300° to 800°C). Leaching studies using simulated fission products indicated that a concentrated phosphoric acid leach was capable of removing 95 to 100% of these materials from such a bed. This acid had the further advantage of yielding a leach liquor which could be converted directly to a phosphate-type glass.

Several experiments were carried out in an effort to encapsulate the Al_2O_3 bed matrices. Materials tested ranged from low melting metals (300°C) to glasses. Best results to date have been achieved with lead silicate glasses (Pemco No. 545). The product is a durable homogeneous mass, the thermal conductivity of which is ≈ 10 times that of bulk aluminum oxide. From the standpoint of more rapid heat dissipation during storage, this increased conductivity is very desirable. Mechanical and chemical testing are now being performed on such materials. Similar encapsulation experiments are being carried out on the sodium fluoride trap material. Preliminary indications are that it also lends itself to fluxing with such glass forming materials.

FISSION PRODUCT RELEASE STUDIES

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This continuing program has as its primary objective an investigation of the chemical states and transport behavior of fission products released from irradiated nuclear fuels under varying conditions of temperature, concentration, and chemical environment. The results of these studies contribute to a fundamental understanding of the fission product release processes, and are needed to predict fission product behavior under a wide variety of potential reactor accident conditions which would be virtually impossible to investigate in large-scale tests.

In addition to the major items discussed below, the following studies were also undertaken as part

of this program: (1) an investigation of the diffusion of iodine in uranium monocarbide, (2) experiments to measure the release rates of iodine from molten stainless steel- UO_2 cermet, (3) the derivation of an analytical equation for predicting fission product deposition in a thermal gradient, and (4) an analytical study of the fundamental processes controlling fission product release rates from molten materials.

Chemical State of Iodine Released From Metallic Uranium and Uranium Monocarbide

This study was undertaken to determine the chemical states of fission products released from fuels at elevated temperatures in He. Although not every species observed at the fuel will be found outside a primary reactor vessel, their identification is important since subsequent reactions usually depend on the initial species evolved. In general, reactions with the fuel are more important than reactions between the fission products.

Experiments were carried out to study the iodine species released from metallic U and hypostoichiometric UC (4.6 wt % carbon) irradiated over the range of 1.0×10^{15} to 5.4×10^{19} nvt. A specific identification of each released species by conventional analytical methods is hindered since the quantities are generally below the picogram level. However, a thermochromatographic technique was found to be useful in studying the semivolatile species. Briefly, the method consists of separating the fission products released from a heated fuel sample by condensing them or their compounds in a quartz tube having a linearly descending temperature profile along the tube wall. The deposition temperature of the fission products is deter-

Figure 21. Deposition of fission-product iodine released into helium.

mined by a gamma-scan of the tube at the completion of an experiment. A combination of techniques involving a neutron activation analysis of the deposits, an observation of the behavior of known species and the effect of varying the chemical environment, together with a thermodynamic analysis of the system, have proved useful in their identification.

The experimental deposition profiles, shown in Figure 21, indicate that at least three distinct iodine species are released from fuel samples heated to temperatures ranging from 1200° to 2500°C. It is evident that the relative quantity of each released species varies with the fuel temperature. Most of the iodine released from molten U at 1240°C deposits at 275°C. As the fuel temperature is raised to $\approx 2000^\circ\text{C}$, a second iodine species which collects below 100°C forms at the expense of the 275°C deposit. At fuel temperatures above 2150°C, a third iodine species, which deposits at $\approx 200^\circ\text{C}$, becomes progressively predominant.

Although Figure 21 shows only the results from the metallic U studies, the same general trend was observed upon heating UC fuels within the temperature range 2300° to $\approx 2500^\circ\text{C}$. In the case of

UC ($\text{mp} \approx 2350^\circ\text{C}$) no experiments were made at temperatures below 2300°C. At temperatures far exceeding 2500°C, the released iodine was observed to collect largely below 100°C.

Earlier studies showed that the iodides were not chemically combined with another fission product. A neutron activation analysis also showed the presence of U in the 275° deposit, although a definite U/I ratio was not established. In addition, speculative thermodynamic calculations indicated that a uranium subiodide such as UI or UI_2 should be stable under these conditions, and should be the major species at 1200°C. A uranium subiodide having a U/I ratio of 1.1 was successfully synthesized by passing elemental iodine tagged with I^{131} over nonirradiated U maintained at 1200°C. This subiodide, carried by a helium stream into the deposition tube, was found to deposit at 275°C. This result suggested that the 275°C deposit from the release experiments was UI or some multiple thereof. The 200°C deposit has not yet been identified, although it is also probably a uranium subiodide. The deposit at 100° and below was found to be essentially elemental iodine.

The temperature dependence of the species discussed above is in qualitative agreement with the behavior of many high temperature systems as explained by Brewer's rule.² Figure 22 is a logarithmic plot of the relative partial pressures of the released iodine species versus $1/T$ constructed by taking the relative partial pressures to be proportional to the peak areas in Figure 21. The three straight lines in this figure show that all of the experimental results up to $\approx 2500^\circ\text{C}$ can be explained solely on the basis of a different heat of vaporization for the individual species. The reason why primarily atomic iodine is released from UC heated to a temperature greatly exceeding its melting point is uncertain. On the basis of this model, it would be expected if the partial pressures of the iodine species are below their equilibrium saturation pressures.

Fission Product Behavior in Sodium

Some studies of fission product retention in sodium have been carried out elsewhere. How-

Figure 22. Relative partial pressure of released iodine species as a function of temperature.

²This rule, based on the fact that the entropies of evaporation of most gaseous species are approximately equal, states that, in general, the relative concentration of a minor species with respect to the major species can often be expected to increase with temperature in a saturated vapor.

ever, there has been no satisfactory interpretation of the data and the quantitative retention characteristics of sodium are still uncertain. Using available thermodynamic data, the probable chemical states and volatility of iodine in sodium were calculated.

A comparison of the estimated standard free energies of formation of the uranium iodides and sodium iodide shows that UI_4 , UI_3 , and UI_2 would undoubtedly react with sodium to form NaI . This is also probably true in the case of some other subiodide such as UI . Similar calculations also showed that compound formation of iodine with other fission products would not be significant where the fission product concentrations are in the order of parts per million. Therefore, iodine is almost certainly chemically combined with sodium in dilute solution.

An estimation of the activity coefficient of sodium iodide in sodium was made by using Wagner's method³ and the Na-NaI phase diagram given by Bredig and Sutherland (ORNL-2548). This expression for the activity coefficient was combined with available vapor pressure data to give the following equation for the partial pressure of NaI in terms of its mole fraction, X_2 , and the temperature, T , in degrees Kelvin.

$$P_{\text{NaI}} = \{1.316 \times 10^{-3} \exp[-(18822/T) + 19.28]\} X_2.$$

(1)

This equation can be used to calculate the partial pressure of sodium iodide in the gas phase which in turn can be related to percentage iodine release knowing the relative volumes of the gas and liquid phases, respectively. A consideration of the standard free energy of formation for NaI shows that dissociation is negligible at least up to 1500°K , and thus the iodine in the gas will be almost entirely NaI .

Using these data, a Rayleigh equation relating the percent vaporization of NaI as a function of the percent Na vaporized, was developed. The equation and a plot for 700° , 800° , and 900°C are shown in Figure 23. It is readily apparent that a significant fraction of the Na can be vaporized without large losses of NaI .

Finally, it is of interest to consider the consequences of oxidizing Na containing iodine. Three

possible reactions with the environment (oxygen and water vapor) are shown in Figure 24. The first reaction has a more positive standard free energy of reaction than the latter two and can be neglected. The standard free energy for the second reaction is the smallest and the reaction appears to be more favorable than the third. It turns out, however, unless a large fraction of the environment is water vapor, reaction 3 actually predominates.

The usual assumption that the activity of the two components Na_2O_2 and NaI are unity suggests that no appreciable decomposition to free iodine takes place. However, it was found experimentally

Figure 23. Calculated equilibrium vaporization of dilute sodium iodide solutions in sodium.

CHEMICAL REACTION	EQUILIBRIUM CONSTANT
(1) $\text{NaI} + \frac{1}{4} \text{O}_2 \rightleftharpoons \frac{1}{2} \text{Na}_2\text{O} + \text{I}$ $\Delta F^\circ_{1000^\circ\text{K}} = 28.82 \text{ kcal/mole}$	$K_1 = \frac{a_{\text{Na}_2\text{O}}^{1/2} \cdot a_{\text{I}}}{a_{\text{NaI}} \cdot a_{\text{O}_2}^{1/4}} = 4.9 \times 10^{-7}$
(2) $\text{NaI} + \frac{1}{4} \text{O}_2 + \frac{1}{2} \text{H}_2\text{O} \rightleftharpoons \text{NaOH} + \text{I}$ $\Delta F^\circ_{1000^\circ\text{K}} = 17.56 \text{ kcal/mole}$	$K_2 = \frac{a_{\text{NaOH}} \cdot a_{\text{I}}}{a_{\text{NaI}} \cdot a_{\text{O}_2}^{1/4} \cdot a_{\text{H}_2\text{O}}^{1/2}} = 1.4 \times 10^{-4}$
(3) $\text{NaI} + \frac{1}{2} \text{O}_2 \rightleftharpoons \frac{1}{2} \text{Na}_2\text{O}_2 + \text{I}$ $\Delta F^\circ_{1000^\circ\text{K}} = 26.93$	$K_3 = \frac{a_{\text{Na}_2\text{O}_2}^{1/2} \cdot a_{\text{I}}}{a_{\text{NaI}} \cdot a_{\text{O}_2}^{1/2}} = 1.2 \times 10^{-6}$
	$P_{\text{I atm}} \approx 5.5 \times 10^{-7} (a_{\text{NaI}} / a_{\text{Na}_2\text{O}_2}^{1/2})$

Figure 24. Reactions and thermodynamic values for the oxidation of sodium iodide (*JANEF Thermochemical Tables*).

³C. Wagner. *Thermodynamics of Alloys*, Addison-Wesley Publishing Co., Inc., Reading, Mass., 1952.

that during the initial stages of NaI oxidation its activity was far less than unity and decomposition of the iodide did indeed take place. An addition of excess Na_2O_2 substantially suppressed decomposition. Therefore, in the case of a reactor environment containing large quantities of Na, also being oxidized to Na_2O_2 , the decomposition of NaI should be negligible and the iodide should concentrate in the condensed phase.

The Chemical States of Iodine Released Into Steam

The chemical states of iodine released from metallic U, UO_2 , and U_3O_8 samples are largely atomic iodine and hydrogen iodide. The relative quantity of each depends on the temperature and the quantity of hydrogen (partial pressure) formed by the metal-water reactions in these systems. Small quantities of iodates and periodates are also formed in solution. In addition, reactions with trace organic impurities were found to result in the formation of organic iodides, particularly methyl iodide. The organic iodides are of particular concern in reactors because of the difficulty in trapping these volatile compounds. Conse-

quently, experiments are under way to study the decomposition of CH_3I as a function of concentration, environment, and radiation dosage. These data are needed to ascertain the stability of CH_3I in a combined high radiation field and oxidizing environment which would exist in a reactor accident.

A series of experiments on the decomposition of CH_3I in air as a function of concentration and gamma-irradiation duration has been completed. Figure 25 shows a series of plots of logarithmic concentration of CH_3I versus irradiation duration. These irradiations were carried out at ambient temperature with a dose rate of 3.48×10^5 rads/hr. The linearity of the plots indicates the decomposition of CH_3I within the concentration range studied (1.58×10^{-8} to 2.42×10^{-7} M) to be pseudo-first-order reaction, with an average half-life of 26 min. Therefore, in the case of a reactor accident, the fraction of iodine existing as methyl iodide should be quite small.

Engineering

HEAT TRANSFER STUDIES

J. CHEN, O. DWYER, M. HELFANT, P. HLAVAC,
M. HORI, C. HSU, S. KALISH, W. YU

In the past year, ~90% of the research studies carried out in the Heat Transfer Group was in the area of liquid metal heat transfer, both single-phase and two-phase. Both analytical and experimental studies were undertaken. The general purpose of this continuing research program is to gain a greater understanding of the science of liquid metal heat transfer under conditions of interest in the nuclear and space fields.

The major accomplishments during the year are summarized below. In addition to these, the study of heat transfer to Hg in flow through annuli continued with measurements of radial velocity and temperature profiles for various radius ratios and Peclet numbers. Design and fabrication of new test sections for the study of heat transfer to liquid metals in (a) 45° cross flow through rod bundles, and (b) in-line flow through eccentric rod bundles were pursued. The Heat Transfer Group also carried the main responsibility for the publication of the *High-Temperature Liquid-Metal Technology Review*, with Dr. O.E. Dwyer serving as editor.

Figure 25. Decrease of CH_3I concentration as a function of irradiation duration.

The work of the Heat Transfer Research Group was aided during the year by the efforts of Mr. Masao Hori, a guest engineer from the Japanese Atomic Energy Research Institute.

Heat Transfer Studies With Boiling Liquid Metals

A project is under way to obtain fundamental heat transfer and fluid dynamic information on convective boiling of liquid metals. The information is required for the design of nuclear power plants which use alkali metals as working fluids in Rankine cycle systems. The experimental work of this project utilizes a forced-convection loop for tests with boiling potassium. The immediate objectives are to measure boiling heat transfer rates, coefficients, pressure drops, and temperature profiles for axial vertical two-phase flow in a round tube. Two series of experiments have been carried out and the ranges of operating variables are tabulated below.

Experimental Variables in Boiling K Tests

	Series I	Series II
Boiler diameter, in.	0.622	0.300
Mass flow velocity, lb/hr-ft ²	3 to 10 × 10 ⁵	4 to 8 × 10 ⁵
Vapor quality at test section, %	0.7 to 16.9	1.9 to 9.4
Max heat flux at test section, Btu/hr-ft ²	81,700	91,500
Boiling temperature, °F	1510 to 1650	1370 to 1515
Boiling pressure, psia	28 to 42	12.2 to 9.4

In the first series of experiments 12 thermocouples were used to measure temperatures at various radial positions in the boiling test section wall, and three in-fluid thermocouples were located at the axis of the boiler to measure fluid temperature. The use of all thermocouples at one axial position enabled the radial temperature profile to be determined with good precision. Results from the first series of tests indicated that for certain conditions of boiling two-phase flow the fluid core temperature was higher than the inside wall temperature. The runs with these negative temperature differences were first thought to be in error, but repeated checks of the experimental method and equipment served only to verify the phenomena. Moreover, runs with single-phase flow gave positive temperature differences of up to 30°F as would be expected. The measured single-phase Nusselt numbers were in good agreement with other recent data and theoretical predictions. It was finally concluded that the observed nega-

Figure 26. Temperature profiles in boiling two-phase flow.

tive temperature differences in two-phase flow represent a true phenomenon.

A theory has been proposed to explain this inverse radial temperature profile, based on the hypothesis that the two-phase fluid is in a non-equilibrium thermodynamic state. Figure 26a shows the postulated radial temperature profile. Under conditions of the experimental tests, two-phase flow would be of the annular type where the vapor flows in a central core (with varying amounts of entrainment) and the liquid flows in an annular film on the pipe wall. With net heat input there must be a temperature drop through the liquid film to a vapor-liquid interface temperature which would be close to, or equal to, the saturation temperature, T_s . Since the measured core temperature, T_o , is higher than the i.d. wall temperature, the profile must then necessarily invert and rise from the value T_s at the interface to the value T_o at the center line. The mechanism causing the vapor core to be at this higher temperature, nonequilibrium state can be found in an examination of the axial temperature profiles along the boiler, as shown in Figure 26b. Associated with the pressure drop through the boiler is a

corresponding decrease of saturation temperature from inlet to outlet. As the vapor flows through the boiler it sees a cooler liquid annulus and must necessarily give up sensible heat, cooling as it flows through the boiler. Where there is high slip and high vapor velocity, it is conceivable that the vapor reaches the measurement point from an upstream higher temperature point before it can reach thermodynamic equilibrium with the local saturation temperature and pressure. The heat transferred to the liquid from the wall is converted into latent heat by bubble nucleation and growth and by evaporation at the liquid-vapor interface.

Figure 27. Temperature profiles in Test Section II of the boiling potassium loop.

Figure 28. Two-phase pressure drop for potassium.

This combination of heat transfer from the wall to the liquid annulus and nonequilibrium cooling of the vapor core could then cause the observed inverse temperature profile. Because of the associated physical properties this nonequilibrium effect would be more important for boiling liquid metals than for other fluids. This effect has not been observed heretofore because in previous experiments with liquid metal no attempts were made to measure the two-phase fluid core temperature.

The second series of experiments, using a different test section, was carried out to test the validity of the above hypothesis. In this test section two in-fluid thermocouples were located at the same axial plane but at different radial positions: one at the center line to measure core temperature, T_o , and the second against the inside diameter to measure temperature of the fluid film near the wall, T_f . Results indeed verified the existence of an inverse temperature profile with boiling two-phase flow. Figure 27 shows the types of temperature profiles measured in the wall and in the fluid for both single-phase and two-phase heat transfer. In the first case, the core temperature is seen to be lower than the film temperature, giving a normal temperature profile, while in the second case the core temperature is measured to be higher than the film temperature, indicating the existence of an inverse temperature profile.

Some results of two-phase pressure drop measurements are shown in Figure 28. The ratio of frictional pressure gradients for two-phase flow and equivalent single-phase flow is plotted against the reciprocal Martinelli-Nelson parameter. For the quality range tested the results are seen to be in good agreement with the standard Martinelli-Nelson correlation, which was originally based on non-liquid-metal results.

Heat Transfer to NaK in Cross Flow Through a Bundle of Circular Rods

Four investigations⁴⁻⁷ of this case have been reported in the literature for Hg and Na and they are all in fairly good agreement. However, in none

⁴V.I. Subbotin, V.E. Minashin, and E.I. Deniskin. *Teplofizika Vysokikh Temperatur* 1, 238 (1963).

⁵V.M. Borishansky, A.A. Andreevsky, and V.B. Zhinkina. *Atomnaya Energiya* 13, 269 (1962).

⁶R.J. Hoe, D. Dropkin, and O.E. Dwyer. *Trans. A.S.M.E.* 79, 889 (1957).

⁷C.L. Rickard, O.E. Dwyer, and D. Dropkin. *Trans. A.S.M.E.* 80, 646 (1958).

of the studies were all the rods in the bundle heated. Therefore, it was decided to carry out a new study at BNL in which all the rods could be heated at the same heat flux, to see what, if any, the difference would be between the two types of operation.

During the past year local and rod-average heat transfer coefficients were determined for 90° cross flow of NaK through a 63-rod bundle (½-in.-o.d. rods, 7 across and 9 deep). The rods were 7 in. long and spaced in an equilateral triangular array where the pitch:diameter ratio was 1.75. There were 8 instrumented test rods distributed throughout the bundle.

Some typical results, for a rod in the interior of the bundle, are shown in Figure 29, where they are compared with the results of previous investigators. Curve A-A represents the results of Subbotin et al. for Hg, where only the test rod was heated, and where the test rod and adjacent rods were heated. It was found that heating adjacent rods had a negligible effect on the average coefficient. Curve B-B represents the experimental results of Borishansky et al. for Na, where the test rod and adjacent rods were heated. Curve C-C is based upon the experimental results of Rickard et al. for Hg, where only the test rod was heated. Curve D-D represents the theoretical curve derived by Hsu⁸ at Brookhaven.

It is seen that at the lower Peclet range there is a distinct difference in the average heat transfer coefficient, depending on whether only the test rod is heated or whether all the rods are heated. For example, at a Peclet number of 50, the coefficient is about 30% lower when only the test element is heated. This difference gradually decreases with increase in Peclet number, until at 200 there is no significant difference. These results are somewhat surprising, but they are found to be easily reproducible. As expected, the agreement between the results of the different investigators improves as the Peclet number is increased. This general trend was shown at all the test rod locations.

Study of Flash Vaporization at Orifices

A small-scale experimental study is under way to determine the characteristics of flash vaporization with flow through an orifice. Flashing orifices have found application in boiling liquid metal loops as a means for circumventing nucleation difficulties. The purpose of this current study is to de-

Figure 29. Average Nusselt number for cross flow of NaK through a staggered rod bundle. A-A, Subbotin et al., ref. 4; B-B, Borishansky et al., ref. 5; C-C, Rickard et al., ref. 7; D-D, Hsu, ref. 8.

termine the variables governing the inception and cessation of flash vaporization and to observe two-phase flow patterns immediately downstream of the orifice. Such information would be helpful for the design and operation of flashing orifices in convective boiling liquid metal systems. The tests are being performed with water at ≈ 1 atm pressure.

The experimental equipment was designed and fabricated during this report period and to date data have been obtained for orifices of diameter ratios 0.407 and 0.161. Measurements of flash inception, flashing pressure drop, downstream pressure recovery, together with photographic records of flashing flow patterns were obtained.

Analytical Study of Heat Transfer to Liquid Metals Flowing In-Line Through Unbaffled Rod Bundles

The purpose of this work was to calculate local and rod-average heat transfer coefficients for turbulent, in-line flow through closely spaced rod bundles. The results are relevant to the design of fuel element assemblies for advanced sodium-cooled fast breeder reactors. The boundary conditions were uniform heat flux and fully developed velocity and temperature profiles. Rod spacing was equilateral triangular with pitch:diameter ratios ranging from 1.100 to 1.375.

⁸C. J. Hsu, *Intern. J. Heat Mass Transfer* 7, 431 (1964).

Table 12

θ , degrees around circumference of rod from point of closest proximity to the next rod	$(t_w - t_w, 30)/(\bar{t}_w - t_b)$	Local h
0	0.481	16000
1.875	0.479	16100
5.625	0.461	16546
9.375	0.404	17650
13.125	0.285	19328
16.875	0.1757	21580
20.625	0.0869	23844
24.375	0.0343	25420
28.125	0.00202	26500
30	0.00000	26750

A typical set of results is given in Table 12 for the case of $P/D = 1.200$, $Pe = 100$, and $Pr = 0.00735$. In the table, t_w = wall surface temperature at angle θ , $t_w, 30$ = wall surface temperature $\theta = 30^\circ$, $\bar{t}_w$ = average surface wall temperature, t_b = bulk temperature of flowing stream, and h = Btu/hr ft².

At low P/D spacings, i.e., in the range investigated, it was found that the relative circumferential temperature variation is essentially independent of heat flux and Peclet number. It depends primarily on the P/D ratio.

It was also found that from a thermal stress standpoint, the absolute temperature variations around the circumferences of the rods do not appear to be intolerably large. For example, at $P/D = 1.100$, $Pe = 200$, and a heat flux of 10^6 Btu/hr-ft², the maximum temperature difference on the rod surface would be $\approx 100^\circ\text{F}$.

The circumferential variation in the local heat transfer coefficient is very dependent on the P/D ratio. At $P/D = 1.375$, the coefficients were found to vary by a factor of ≈ 1.2 , at 1.200 by ≈ 1.7 , and 1.100 by ≈ 100 . Below $P/D \approx 1.3$, the rod-average heat transfer coefficient drops increasingly fast as the P/D ratio approaches 1.000.

Analytical Study of Heat Transfer to Liquid Metals Flowing in Eccentric Annuli

The purpose of this study, completed during this fiscal year, was to determine the effect of eccentricity on the local and average heat transfer coefficients for liquid metals flowing through eccentric annuli. These results have bearing on the problem of eccentricity in rod bundles. The boundary conditions for this analytical study were

Table 13

Heat Transfer for Flow Through Eccentric Annuli				
R	e	$\bar{\psi}Pe$	Nu	Nu/Nu_0
1.5	0.15	368	6.89	0.895
		1700	11.43	0.950
	0.30	368	5.91	0.767
		1700	9.61	0.798
		8000	19.23	0.737
	0.50	368	4.58	0.596
		1700	7.27	0.604
	0.70	368	3.47	0.451
		1700	6.24	0.518
		8000	14.43	0.553
2.5	0.30	1700	11.25	0.818
	0.70		7.13	0.519
4.0	0.30	1700	13.45	0.851
	0.70		8.17	0.517

(a) heat transfer from the inner wall only, (b) constant circumferential inner wall temperature at a given axial position, (c) for a given angle on the circumference of the inner wall the heat flux is uniform with length, and (d) the velocity and temperature profiles are fully developed. The results are summarized in Table 13, where $R = r_2/r_1$, e = eccentricity, $\bar{\psi} = (\epsilon_H/\epsilon_M)av$, Pe = Peclet number, $Nu = (hD_e)/k$ = Nusselt number, and Nu_0 = Nusselt number for concentric case. It is instructive to compare them with those for the case of uniform heat flux, previously studied by the Heat Transfer Research Group. In the present case, it was found that the reduction in the average heat transfer coefficient was much less dependent on the radius ratio, r_2/r_1 . For example, at $\bar{\psi}Pe = 1700$, and $e = 0.30$, the value of Nu/Nu_0 in the present case changes only from 0.85 to 0.80 as r_2/r_1 is reduced from 4.0 to 1.5, while for the same conditions the corresponding Nu/Nu_0 ratios are 0.82 and 0.32, respectively, in the case of uniform heat flux. The explanation for this is found in the fact that, in the present case, the heat transfer through the flowing stream assumes a fairly radial pattern for all r_2/r_1 ratios.

In general, it can also be concluded that, in the present case, the reduction in the average heat transfer coefficient due to eccentricity is usually considerably less than that found in the case of uniform heat flux.

Figure 30. Laminar heat transfer in tubes with convective boundary condition.

Analytical Study of Heat Transfer in Laminar Flow With Convective Boundary Conditions

The purpose of this study is to obtain an analytical solution to the problem of entrance region heat transfer in laminar flow with convective heat transfer taking place through the channel wall. Complete solutions were obtained for both flow inside a tube and flow between parallel plates. Figure 30 illustrates the variation of local Nusselt number with axial position for the case of pipe flow for various values of the convective parameter, Δ , defined as follows.

$$\Delta = hr_o k,$$

where h = over-all heat transfer coefficient based on the resistance of pipe wall and that between the pipe wall and the surrounding medium, r_o = radius of a pipe, and k = thermal conductivity of fluid.

Analysis of Liquid Metal Heat Transfer in Tubes With Radiant Cooling

An analytical study was initiated and completed in this report period to determine the heat transfer characteristics of liquid metals flowing through tubes which are radiantly cooled. This problem arises in nuclear power systems for space applications where the ultimate heat sink is a radiator.

For this problem, the wall heat flux is prescribed as being proportional to the fourth power of the local wall temperature. The governing heat transfer equations, for the laminar flow case, are

$$\tau_w(x, \alpha) = 1 - \alpha \int_0^x \times \left\{ 4 - \sum_{n=1}^{\infty} C_n R_n \beta_n^2 \exp[-\beta_n^2(x-x')] \right\} \tau_w^4(x') dx', \quad (1)$$

$$\text{Nu}(x, \alpha) = \frac{2\tau_w^4(x)}{-\int_0^x \tau_w^4(x') \sum_{n=1}^{\infty} C_n R_n \beta_n^2 \exp[-\beta_n^2(x-x')] dx'}, \quad (2)$$

where

$$\tau_w(x, \alpha) = T(x)/T_o,$$

T_o = entrance temperature,

$x = Z/(\text{Re} \cdot \text{Pr} \cdot R)$,

R = radius of tube,

$\alpha = (\epsilon \sigma T_o^3 R)/k$,

Z = axial coordinate, and

β_n, R_n, C_n = eigenvalues, eigenfunctions, and eigenconstants for constant heat flux case.

An approximate solution to this system of non-linear integral equations has been found in terms of the Liouville-Neumann series. Exact results were also obtained by iterative numerical solution.

The results show that for any given value of the radiation parameter, α , the local heat flux diminishes sharply in the initial length of the tube. Thus for $\alpha = 0.5$ the local heat flux at an axial position of $x = 0.01$ is only 65% of its value at the entrance.

Analytical Study of Nonequilibrium Two-Phase Flow

A project was initiated to develop the theory of nonequilibrium two-phase flow, following the concepts introduced in the boiling potassium experimental program described above. The objective is to derive a theoretical expression for the inverse temperature profile in a two-phase liquid-metal stream by analyzing the process of simultaneous heat and mass transfer in the vapor core with axially varying saturation temperatures. In the first part of the project, the problem was limited to the case of uniform velocity in the core, uniform vaporization, and a step change in saturation temperature. For this case the governing equations are

$$u = \text{axial velocity} = u_o - (2v_w/r_o)x,$$

$$v = \text{radial velocity} = (r/r_o)v_w,$$

$$\rho C p [u_o - (2v_w/r_o)x] \frac{\partial T}{\partial x} +$$

$$\rho C p [(r/r_o)v_w] \frac{\partial T}{\partial r} = \frac{1}{r} \frac{\partial}{\partial r} \left(kr \frac{\partial T}{\partial r} \right),$$

with boundary conditions

Figure 31. Temperature profiles in nonequilibrium vapor core.

$$\begin{aligned}
 T &= T_0 \text{ at } x \leq 0, \\
 T_s(r=r_0) &= \text{a constant at } x \geq 0, \\
 v &= v_w \text{ at } r=r_0 \text{ (} v_w \text{ is negative for mass addition),} \\
 (dv/dr) &= 0 \text{ at } r=0, \text{ and} \\
 u &= u_0 \text{ at } x \leq 0.
 \end{aligned}$$

After separation of variables this system leads to a confluent hypergeometric differential equation. Numerical solution of the radial equation was used to obtain the necessary eigenvalues. Results have been computed for $\beta = 0, -1, -3$, and -5 where the vaporization parameter, β , is defined as

$$\beta = (C_p \rho / k) v_w r_0$$

where r_0 = radius of vapor core, v_w = radial velocity at r_0 caused by vaporization of the liquid annulus, C_p = heat capacity of the vapor, ρ = density of vapor, and k = thermal conductivity of vapor.

Figure 31 shows sample temperature profiles in the vapor core obtained from this solution, for the case of $u_0 = 10$ ft/sec, $x/r_0 = 100$, and four different values of β . It is seen that for the same entrance velocity, higher vaporization rates (higher β) lead to higher center line temperatures at a given axial position. This is attributable to the increase in average local velocity with increased mass addition by vaporization.

MISSILE PROPULSION REACTOR

L. HATCH, G. LINDAUER, E. WIRSING, M. ROSSO

Rotating Fluidized Bed

A major problem in the development of very high power density nuclear reactors for applications such as in rocket propulsion is the provision for transfer of heat at the very high fluxes required from the fuel to the gaseous coolant. In the conventional solid fuel element reactor concept a conflict is posed between the requirements for large surface area for heat transfer and for structural integrity of the fuel element. In an attempt to resolve this conflict, a study is being performed to investigate the feasibility of developing a reactor design based on the utilization of solid fuel in granular form. The concept features a bed of granules in the form of a rotating cylindrical annulus with the coolant flowing radially inward through the bed with sufficient velocity and drag force to fluidize it. Fuel in the form of small particles would present large specific area for transfer of heat, and coolant velocities through the bed could be very high because of centrifugal force.

Initial investigations have been centered on (1) qualitative evaluation of the physical behavior of gas fluidized beds subjected to high g forces and high flow rates, (2) determination of performance characteristics of fluidized beds under high g 's with respect to gas flow rates, and (3) determination of particle-to-fluid heat transfer coefficients in packed and fluidized beds at very high gas flow rates.

Gas fluidized beds under high g 's with sharp density gradients in the gas with concurrent linear velocity gradients present unusual problems not encountered at 1 g . For example, fluidization begins at the downstream face and extends upstream as the flow is increased. Thus the bed may be in a state of partial fluidization or complete fluidization. When the flow is increased to that at which the entire bed is fluidized, the downstream velocity

Figure 32. Cutaway section of rotating fluidized bed assembly.

might be more than an order of magnitude higher than the minimum fluidization velocity. Since a large increase in linear velocity of the bed would be accompanied by a corresponding increase in drag force, a relatively high degree of bed expansion would be expected to occur in the downstream region. In 1-*g* systems highly expanded gas fluidized beds usually show substantial gas pocket or bubble formation. It is necessary therefore to determine whether bubble formation would be an adverse limiting factor under conditions required for high power density reactor operation.

Physical Behavior and Performance Characteristics of Fluidized Beds Subjected to High *g*'s

Two methods were used to determine the extent of fluidization of the rotating particulate beds. One method involved the determination of the extent of backmixing of darkened particles, added at the downstream face, in a bed of identical but colorless particles. The other method was based on the relationship between gas flow rate and pressure drop through the bed.

The apparatus used consists primarily of a vessel which is rotated at speeds up to 5000 rpm and which contains the bed of particulate material. A side view and cross section of the vessel are shown in Figure 32 with indicated direction of gas flow. The particles making up the bed were spherical glass beads with a density of 2.5 g/cc. Two particle size ranges were used, namely 88 to 125 and 420 to 500 μ .

The qualitative study of bed behavior was made primarily by means of high speed photography.

Darkened beads were used to provide a means of measuring the extent of particle intermixing.

After a uniform bed of clear beads was established, the dark beads were added to form a thin layer at the downstream face. Air flow was increased until migration of the dark beads into the clear beads could be observed. The point at which fluidization extended to the upstream face of the bed was not well defined by the visual method. At this point, however, the pressure drop became constant with increasing flow. This discontinuity in the pressure drop-flow relationship established the point of reference for minimum fluidization.

In the experiments at very high *g*'s (3450) partial fluidization could be easily obtained with very little unevenness along the interface defined by the dark beads. At lower *g*'s (138) gross unevenness existed at the interface.

In several experiments using 190-g beds (≈ 0.25 in. deep) it was possible to achieve complete backmixing without evidence of bubbling in the bed. For all beds deeper than 0.25 in., complete backmixing could not be obtained without bubbling. The greatest depth of backmixing without bubbling was 0.34 in., obtained with a 0.5-in.-deep bed.

Figure 33 correlates the Reynolds number and drag force at which fluidization at the upstream bed surface began at high g 's. The correlation is a plot of one function of Reynolds number and drag force as ordinate which is directly proportional to the superficial gas velocity versus a second function of Reynolds number and drag force as abscissa which is directly proportional to the particle diameter. The dotted line is a correlation made with a rotating tube at Los Alamos and the solid line a correlation of BNL data. The flow rates at which complete backmixing occurred were compared with the minimum flow rates at which complete fluidization occurred as determined by pressure drop measurements. It was concluded that no satisfactory agreement was found.

Heat Transfer Determination

For the reactor system under investigation, it is considered that heat transfer coefficients as high as 1000 Btu/hr-ft²-°F may be required. Both partially and completely fluidized beds operated at

Figure 33. Correlation of minimum fluidization data at high g 's.

high g 's are being considered for nuclear rocket applications, and therefore determinations of heat transfer coefficients in packed and fluidized beds are involved. An experimental program has been initiated to measure heat transfer coefficients using the cyclic heating method. A gas whose temperature varies periodically with time is passed through a bed of particles. Heat is transferred out of the gas to the particles during one part of the cycle and returned to the gas during the other part of the cycle. The rate of heat transfer depends on the temperature difference between the particle surface and the gas stream at each point. The cyclic temperature wave in the gas leaving the bed will be lower in amplitude than, and exhibit a shift in phase from, the incoming wave. Heat transfer coefficients can be calculated from this phase shift and decrease in amplitude of the gas leaving the bed.

The experimental system for measuring heat transfer coefficients has been completed and preliminary tests have been made which indicate that the apparatus operates satisfactorily over a frequency range of 0.05 to 30 cycles/sec.

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Radiation Division

B. MANOWITZ

Radiation Research

D. BALLANTINE

SOLID-STATE REACTIONS

The previously reported work on trioxane polymerization in the solid state emphasized the difficulty of obtaining reproducibility, the effect of pressure on the rate and extent of reaction, and the possible effect of defects on the polymerization.

During the past year the effect of pressure has been investigated more extensively and has shown that samples pressurized prior to irradiation always exhibit a higher equilibrium degree of polymerization and a higher initial rate. Typical curves for pressed and unpressed series of samples are shown in Figure 1.

It has also been observed that there is a relationship between the amount of free volume associated with a sample and the degree of polymerization. Thus equal weights of trioxane gave higher yields when irradiated in filled 2-ml bottles than in partially filled 4.5-ml bottles. Figure 2 demonstrates the magnitude of this effect. These results, in conjunction with the experiments on the effect of pressure where free volume is minimized, suggest that sublimation plays a significant role in the process. The results can very naively be explained by postulation of formation of initiating sites at surfaces which can be destroyed by a sublimation controlled recombination in the vapor phase or at a surface.

It has also been found that the equilibrium degree of polymerization depends on irradiation dose rate being higher at the higher dose rates. The precise explanation for this is not immediately obvious.

Recently polymerizing trioxane crystals have been studied by polarized light and phase contrast microscopy with interesting results. It has been found that reaction seems to initiate at the surface of crystals, propagate across crystal interfaces, and in propagating across crystal interfaces continue to grow in a direction dictated by the polymer's crystal habit rather than along the *c*-axis of the second crystal. Figure 3 is a phase photomicro-

graph of partially polymerized trioxane. The bright area shows crystalline monomers with the *c*-axis parallel to the plane of the photomicrograph. The dark area shows monomer with the *c*-axis perpendicular to this plane. The threadlike films are crystalline polymer. It can be seen that the polymer fibers are parallel to the *c*-axis in the bright area but have continued at right angles to the *c*-axis in the dark area.

Electron spin resonance (ESR) studies of solid solutions of acrylamide in propionamide provide further confirmation that between -150° and -30°C the first monomer addition is in a given crystallographic direction (the screw axis direction). Above -30°C the further addition steps become random in direction. However, the evidence is that above -30°C even the first addition step can be in directions other than the screw axis but the probability of this is lower.

It has previously been shown that oxygen will diffuse into dilute solid solutions of acrylamide in propionamide and at the same time will markedly reduce the amount of polymerization that takes place. It has now been shown that the polymerization which does occur is due to the relatively slow rate of diffusion of the oxygen into the lattice. If the reaction is carried out under conditions where the rate of oxygen diffusion is no longer limiting, the polymerization is almost completely suppressed even in solid solutions fairly concentrated in acrylamide.

ESR measurements are now being made on other solid amides. The linear amides are known to have crystal structures similar to propionamide and acrylamide. Those that have been studied, when irradiated at low temperatures, show ESR spectra that seem characteristic of a mixture of free radicals. However, when the crystals are warmed to some intermediate temperature and recooled, they show only spectra characteristic of radicals with the odd spin on the carbon alpha to the amide group. Isobutyramide, which is the only branch chain amide studied thus far, shows similar effects. These spectral changes apparently occur without any great loss in radical population. This

Figure 1. Effect of pressure on polymerization of trioxane.

is indicative of some sort of hydrogen migration mechanism within the crystal.

Since the crystal structure of the linear amides is similar to propionamide, it was felt that their behavior with respect to oxygen should be similar. It has now been shown that oxygen can also diffuse through these crystals and scavenge free radicals. As in propionamide, it is believed that the oxygen diffuses through defects and between the planes of the crystal structure. In principle, this diffusion should be hindered because of chain branching in isobutyramide. It has now been shown that the diffusion of oxygen, as reflected by the rate of radical scavenging, is much slower in isobutyramide than in *n*-butyramide or propionamide. The crystal structure of isobutyramide is now being studied.

D. BALLANTINE, G. ADLER, J. PETROPOULOS,
W. REAMS, A. NELSON

POLYMERIZATION MECHANISMS

The kinetic behavior of the radiation-induced polymerization of carefully purified and dried liquid styrene has been found to depend critically on the residual water content of the monomer and the reaction vessel walls. All previously reported data on this monomer had indicated a square-root dependence of rate of polymerization on dose rate, with rates of the order of 10^{-5} moles/liter/sec at

Figure 2. Effect of ratio of sample size to free volume on polymerization of trioxane.

Figure 3. Phase contrast photomicrograph of partially polymerized trioxane.

Table 1
Gas Yields From Tolunitrile and
Tolualdehyde Radiolysis (Liquid)

	Ortho	Meta	Para
<u>Tolunitrile</u>			
$G_{\text{total gas}}$	0.067	0.21	0.057
G_{H_2}	0.054	0.042	0.045
G_{CH_4}	0.003	0.002	0.004
G_{N_2}	0.001	0.19	0.006
<u>Tolualdehyde</u>			
$G_{\text{total gas}}$	0.24	0.33	0.21
G_{H_2}	0.089	0.099	0.083
G_{CH_4}	0.002	0.058	0.002
G_{CO_2}	0.013	0.072	0.013
G_{CO}	0.14	0.075	0.11

0°C and 10^5 rads/hr. With careful drying techniques, including baking all glassware at 500°C for 24 hr at 10^{-8} mm pressure, rates of polymerization as high as 10^{-2} moles/liter/sec have been obtained at this temperature and dose rate. By varying the exhaustiveness of the drying technique, rates between these extremes can be achieved.

In addition to increasing the absolute value of the rate of reaction, increased drying of the sample also causes differences in the order dependence of the polymerization on the dose rate. As the samples are successively dried to a greater and greater extent, the order dependence shifts from square-root through intermediate values until it achieves a linear dependence and then reverts to approximately a square-root dependence at the very high absolute value of rates. This appears to suggest that as water is removed, the mechanism changes from a preponderance of free radical propagation (low rate, square-root) to cationic (higher rate, linear) and then to simultaneous cationic and anionic propagation (higher rate, square-root). The same type of behavior is exhibited by α -methylstyrene.

It has been demonstrated that the method of sample preparation does not affect either the thermal rate of polymerization of styrene or that obtained by ultraviolet initiation. Thus, the effects observed are unique to the radiation-initiated reaction.

Recently an investigation of the intermediates formed in these monomers has been initiated using pulse radiolysis techniques with the cooperation of

personnel at Argonne National Laboratory. These data, although incomplete, are not inconsistent with the above hypothesis.

Studies of the electrical conductivity and dielectric behavior of dilute solutions of sodium anthracide in tetrahydrofuran, as a function of temperature and frequency, are still in progress. The data have not yet been fully analyzed.

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

RADIOLYSIS OF AROMATIC COMPOUNDS

The study of substituted toluenes has been continued to include all three isomers of tolualdehyde, tolunitrile, nitrotoluene, and toluidine. In addition to these compounds, mesitylene and ethyl benzene are being investigated.

Table 1 shows the results obtained for tolunitrile and tolualdehyde, respectively.

Analysis of the data in Table 1 indicates a very strong isomer effect when an electropositive substituent is meta to the methyl group in substituted toluenes. Although an isomer effect has been noticed in the electronegatively substituted toluenes it was not as pronounced as in these cases. Further study will be required before definite conclusions can be drawn from the data. Plans are under way to look at some disubstituted toluenes to see if the isomer effect can be enhanced or diminished.

The data for the other compounds being investigated are still incomplete because of analytical difficulties.

A simple apparatus has been used to do some preliminary fission fragment radiolysis studies on toluene. It is relatively simple to separate the irradiated toluene from the uranium-palladium fission foil and to measure radiolysis gases and reaction products. Fragmentary analyses indicate that polymeric product yields are much lower than in the radiolysis with gamma rays but that low boiling products may be formed in higher yields.

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N. CARCIELLO

Radiation Processing

M. STEINBERG

CHEMONUCLEAR PROGRAM

The purpose of the chemonuclear program is to perform basic and applied research and general

development of the use of reactor radiation for the synthesis and production of industrial chemicals. Work is performed in the radiation and fission fragment chemistry of promising reactions, the development of thin chemonuclear fuel, and the design and evaluation of complete chemonuclear reactor and process systems. A major portion of the effort has been involved in the design, construction, installation, and eventual operation of the Chemonuclear In-Pile Research Loop (CIRL) which will serve as a research tool to carry out the above program.

Radiation Chemistry Studies

Fixation of Nitrogen in the Nitrogen-Oxygen Systems. The yield *vs* dose curve at 68 atm has been evaluated in detail (Figure 4). Thin U-Pd foils were used as a source of fission fragments in these studies. At very high doses ($\approx 75 \times 10^{22}$ eV/sample) sufficient NO_2 is made so that liquid N_2O_4 condenses in the capsule during the irradiation, and an apparent increase in $G(\text{NO}_2)$ is observed while the N_2O concentration has already reached a steady state. Although it is apparent that more accurate experimental results are needed, it is interesting to note that in the dose range 100 to 110×10^{22} eV/sample, NO_2 is being formed with a G value of 3 to 9. At the highest dose given to the sample, $\approx 2\%$ of the oxygen remains in the system.

Capsules containing a N_2 - O_2 mixture (77.3% N_2 -22.7% O_2) under pressures in the range 4.8 to 66.8 atm have been irradiated for 1 hr in the

Figure 4. Fission fragment plus reactor irradiation (n , p , and γ) of a 77.3% N_2 -22.7% O_2 gas mixture.

Table 2

Initial pressure, atm	$G(\text{NO}_2)_T$	$G(\text{N}_2\text{O})$	$G(\text{NO}_2)_T + G(\text{N}_2\text{O})$
4.8	0.76	0.69	1.45
6.3	0.88	0.52	1.42
17.0	1.20	0.41	1.61
24.1	1.03	0.44	1.47
41.8	1.12	0.33	1.45
51.8	1.28	0.26	1.54
64.8	1.21	0.27	1.48

Brookhaven Graphite Research Reactor (BGRR). The volume of the vessels and the weight of U-Pd foils were kept constant. The results are tabulated in Table 2, and it is observed that $G(\text{NO}_2)_T$ apparently increases while $G(\text{N}_2\text{O})$ decreases, the greater the initial pressure in the capsule. Although the fission fragment energy input was kept constant, the energy absorbed from the n , p , and γ modes of energy deposition increases with pressure, e.g., at 5 atm it is some 3% of the total energy absorbed while at 65 atm pressure it is $\approx 25\%$. The changes in the $G(\text{NO}_2)_T$ and $G(\text{N}_2\text{O})$ values as a function of pressure may be due to the differences in concentration of products in these experiments.

Experiments were initiated in which a 100-cc volume was irradiated with Co^{60} γ energy at a dose of 6.79×10^5 rads/hr while N_2 - O_2 gas flowed through the vessel. The gases are continually analyzed in a photoanalyzer and a chromatograph. Preliminary results indicate that at high flow rates ozone is present, NO_2 does not appear, and there is < 100 ppm N_2O present. At low flow rates, O_3 decreases to negligible values, NO_2 begins to appear, and the N_2O is still undetectable. Under static conditions at higher doses, the N_2O appears in addition to the NO_2 . A maximum $G(\text{O}_3) = 1.89$ was obtained at 680 atm pressure. The $G(\text{NO}_2)$ is about 1.13 at 68 atm pressure and decreases somewhat to about 1.03 at 680 atm pressure. The highest O_3 content attained was about 300 ppm. Additional experiments are being carried out to determine whether a reaction between N_2 and N_2O_4 can take place giving rise to N_2O_3 in a radiation field at high pressures.

N_2O Dosimetry. A characteristic of a good chemical dosimeter is that of simplicity. The following method has been adopted and evaluated for the N_2O dosimeter. N_2O at an accurately known pressure of ≈ 5 atm is irradiated in a stan-

dard Al capsule and the N_2 content analyzed by bleeding the gas at 1 atm pressure into a gas sampling valve of a gas chromatograph. In this way at least three measurements of the volume percent N_2 can be made per exposure and the postirradiation handling of the capsule is reduced to a minimum. A calibration curve of volume percent N_2 vs absorbed dose for Co^{60} γ radiation (absorbed dose being deduced from the Fricke dosimeter) has been measured in detail over the concentration range of N_2 useful for calibrating the U^{235} foil elements. The energy deposited in the gas phase by these elements, as evaluated by the N_2O dosimeter, agrees within experimental error with that calculated by using the accepted analytical expression for the energy loss of fission fragments within the foil.

Ozone Synthesis. The synthesis of ozone by Co^{60} γ irradiation of O_2 has been investigated under the following conditions: dose range, 3×10^4 to 7×10^8 rads; dose rate, 1×10^4 to 10^7 rads/hr; pressure, 300 to 700 mm Hg; ambient pool temperature, $10^\circ C$.

Preliminary experiments showed that quartz and Pyrex vessels gave greater yields than Al vessels. Quartz vessels have been used exclusively in the reported experiments. The highest G value obtained on extrapolation of the yield vs dose curve to zero dose was $G(O_3) = 5.6$, essentially in agreement with previous literature values obtained at room temperature. During most of the irradiation period, while the ozone concentration was increasing to its final steady-state value, the differential $G(O_3)$ value was 1:1.

Figure 5. Dose rate dependence in γ irradiation of oxygen.

A marked dependence of ozone steady-state concentration ($[O_3]_{ss}$) on dose rate was found (Figure 5). This dependence was fitted by the expression

$$[O_3]_{ss} \propto I^{0.83 \pm 0.06}$$

The highest ozone concentration obtained was 0.2% by volume. These results are in disagreement with the postulated ion-chain decomposition back reaction. However, the data are insufficient as yet to elucidate the reaction mechanism.

Additives such as CO , NO_2 , and CF_4 have not been found to increase the ozone yield. Addition of glass wool while decreasing the ozone yield did not completely inhibit its formation.

Fission fragment irradiation with a Cf^{252} isotope source has failed to produce any detectable ozone, apparently because of an efficient catalytic reaction on the metallic walls of the cell. J. SEARS,

J. SUTHERLAND

Radiolysis of Liquid Ammonia. The investigation of the radiolysis of liquid ammonia has continued. In addition to the work on pure ammonia, solutions of the following compounds in the concentration range 10^{-7} to 10^{-3} M have been irradiated; H_2O , N_2H_4 , H_2 , H_2/N_2H_4 , NH_4Cl , KN_3 , and $(CH_3)_3C-OH$. The presence of HN_3 at high doses in the radiolysis of pure ammonia has been confirmed by infrared and near-infrared spectroscopy. When a 10^{-3} M N_2H_4 solution was irradiated, the following values for H_2 and N_2 were obtained: $G(H_2) = 1.10$ and $G(N_2) = 0.46$. When a H_2 , N_2H_4 solution was irradiated the N_2H_4 was decomposed by a chain mechanism, but in the presence of H_2 alone, preliminary experiments showed that the N_2H_4 was protected at low doses. Solutions of NH_4Cl and $(C_2H_5)_3C-OH$ gave apparently larger yields of N_2H_4 in the same dose range as that for pure ammonia. In the case of the alcohol, this has been shown to be due to the presence of an amide interfering with the analytical method for N_2H_4 . H. KRAMER, J. SUTHERLAND

Chemonuclear Fuel Development

Alloys of U and Pd, either bare or with a very thin cladding of Pt, have proven to be well-suited for use as chemonuclear fuel material. Most of the effort has been concentrated on the alloy containing 20% U-80% Pd. While some work has been done with natural U as a stand-in, the alloy to be fabricated into fuel elements has been made up with fully enriched U ($>93.3\%$). It has been pos-

Figure 6. Photomicrograph of section of Pt-clad U-Pd alloy foil. Composite is 0.0001-in.-thick ($2.0\ \mu$), with a 0.00001-in.-thick ($0.25\ \mu$) cladding ($2000\times$).

sible to roll this alloy into foil 0.0001 in. ($2.5\ \mu$) thick. A Pt cladding can be diffusion-bonded to it and the composite also rolled to foil of the same thickness, with a layer of Pt 0.00001 in. ($0.25\ \mu$) thick on either side. Figure 6 shows a photomicrograph of a section of such a clad foil. Average range of a fission fragment in the alloy is about $6\ \mu$, and a value of 35.5% has been obtained with the N_2O dosimeter for the energy deposition efficiency for a sample of the clad material.

Samples of the alloy were irradiated to 25% burnup in the MTR. In an earlier experiment the specimens had been destroyed, but the indications were that this had been caused by thermal overheating rather than by radiation damage. In the second irradiation, duplicate specimens were irradiated, one in the same type holder used in the first irradiation and the other in an improved mount that provided for better heat removal from the foil. The specimens in the original type holder were again destroyed, but those in the improved type appeared unaffected by heat or radiation. Samples (either bare or coated with a thin Al cladding) irradiated in He looked very good. Those coated with a thin film of Al_2O_3 melted, presumably because of the insulating effect of the ceramic coating. Exposed to air or oxygen, the alloy was very slightly discolored. The alloy was badly attacked in NO_2 at 1 atm pressure. There

was no alloy clad with Pt available at the time this irradiation was made but later irradiations of the clad alloy indicated good resistance to corrosion by NO_2 . These latter were not run to high burnups, however. The evidence to date indicates that with a clean alloy core, free from nonmetallic inclusion and with the high-integrity cladding that has been obtained with Pt, the fuel material is extremely resistant to both chemical attack and radiation damage.

A great deal of effort has gone into developing a technology for producing ultrathin chemonuclear fuel. Several melting and casting techniques have been investigated, under vacuum and under reduced Ar pressure, and with consumable electrodes as well as other arc methods. The ingots now obtained are extremely pure and free of inclusions and gas bubbles. A Stanat 2-high-4-high rolling mill has been installed at BNL. This has made it possible to roll foil to 0.005 in. Slabs of alloy are forced into tightly fitting "picture frames" of stainless steel. These frames support the alloy during the initial rolling and prevent the formation of cracks that would ruin the slabs. A Pt cladding sheet is diffusion-bonded to the alloy at an intermediate thickness, usually 0.050 in., by heating the composite to about $850^\circ C$ under pressure in a high vacuum. The 0.005-in. foil is then rolled to the final 0.0001-in. thickness. This is done on highly specialized multiple roll Sundwig or Sendzimir mills. Since this is just about the extreme limit of thinness for a commercial mill, some difficulty is still being experienced at this stage. A serious limitation is the small amount of alloy that can be worked with at a time because of criticality restrictions. It is difficult to set up production-type machines, and a small flaw in the original ingot means the loss of much of the metal in a slab or strip.

The honeycomb configuration has been found to be the most satisfactory one for foil fuel elements. A 5-ft-long element, made up of 2-in.-long units, has been formed of 0.0001-in.-thick Deltamax (a stand-in Fe-Ni alloy material) honeycomb with $\frac{3}{32}$ -in. cells. Some of these units have been exposed to air flowing at 30 ft/sec at $1000^\circ F$ for 1000 hr without experiencing any mechanical damage. The fabricator of the honeycomb, Hexcel Corp., has succeeded in making honeycomb with a 1-mm cell. Since 1 mm represents the average range of a fission fragment in air at 1000 psi and $1000^\circ F$, the enriched U foil will be made up into an element with this configuration.

By informal agreement among the laboratories working in the chemonuclear field, 20% U-80% Pd alloy, 0.0001 in. thick, has been designated as Brookhaven Standard Source No. 1, and the same foil clad with 0.00001 in. of Pt is Brookhaven Standard Source No. 2. Standard samples have been supplied to interested laboratories in this country and negotiations are proceeding for supplying this material to foreign laboratories.

Work on the fabrication of a Pt-clad U-Pd honeycomb element is also under way at the Northwest Pacific Laboratory of Battelle Memorial Institute. Here the fuel and cladding materials are coextruded in a matrix of sacrificial metal that can be dissolved out with acid. Initial results are encouraging.

Work with U glass fibers has been discontinued, since it is evident that the thermally and electrically nonconducting nature of the material makes it highly susceptible to damage by fission fragments. The relatively low melting points add to the unsuitability for service as a chemonuclear fuel. There is still interest in U-containing metal fibers, however.

Geometrical analyses have been carried out to determine fission fragment energy deposition efficiencies for various configurations and foil thicknesses, and the maximum power levels that could be obtained.

An extensive thermal analysis of the honeycomb element is being carried out by C. Hsu of the Chemistry and Chemical Engineering Division to provide a detailed picture of the thermal distributions to be expected in a honeycomb fuel under irradiation in a flowing gas stream.

Chemonuclear In-Pile Research Loop

Work on the CIRL has proceeded steadily in accordance with the program outlined last year. Efforts in the areas of design, development, and fabrication have brought the loop to the point where its final specifications have been fixed and very few unresolved problems remain. Considerable work still remains to be done, however, in completing the fabrication and assembly of the loop and its containment, installing it at the BGRR together with its shielding, and testing it in all phases of its operation before the chemonuclear

Figure 7. Schematic flow sheet of the Chemonuclear In-Pile Research Loop (CIRL).

Figure 8. In-pile section of CIRL being prepared for testing under rated pressure, temperature, and gas flow conditions prior to installation in the BGRR.

experimental program proper can be undertaken. Figure 7 shows a schematic diagram of the CIRL.

The in-pile section of the loop has been installed in a cold test facility (Figure 8) and run under conditions that simulated final operation in all respects except for radiation. Several other loop components were installed in the same facility and tested at the same time. These included the flowmeters, preheater, and some of the remotely operated valves. As a result, the preheater has been reworked to improve its heat transfer characteristics and to increase the amount of heat transfer surface. At the completion of this test, installation of the fuel carriage drive mechanism was begun. When this has been completed, the loop will be rerun to determine its full operating range.

The shielded system for inserting and removing fuel cartridges, at the east end of the in-pile section, has been built and its operation demonstrated satisfactorily. The procedure for removing the in-pile section from the BGRR under emer-

gency conditions with an irradiated fuel cartridge in place has also been demonstrated. This involves cutting the section into short lengths with a 160-ton hydraulic guillotine cutter and putting the pieces into shielded carriers with adequate radiation shielding and contamination control. Figures 9 and 10 show this operation.

A full-scale mock-up of the east face shielding plug was built and inserted into experimental hole E-11 during an annealing run, at about 5% of full reactor power. Measurements made of neutron and gamma levels indicated an adequate shielding design when extrapolated to full power.

The design of the out-of-pile section of the loop has been completed and almost all the components are on site. Fabrication of the piping and components into subassemblies is well under way, and the subassemblies are being mounted on racks which will be placed in the containment tanks. Because of the complexity and compactness of the design, many details have been mocked-up to en-

Figure 9. Sketch of the guillotine cutter designed to facilitate the eventual removal and disposal of the in-pile section of the CIRL.

Figure 10. Guillotine cutter simulating disposal of full-scale mock-up of in-pile section.

sure adequate space and accessibility for performing required operations. Models were built to demonstrate large-scale operation capability.

The only major components for the loop still undelivered are the two gas-bearing compressors that will circulate the process gas. The novel designs, resulting from the wide range of operating conditions, corrosion resistance, and process-gas cleanliness required, have resulted in considerable delays in the completion of the machines by the respective manufacturers. It is believed that all of the technical problems have been solved and the machines will be ready for final testing shortly.

Shielding for the loop has been designed and the required materials are on site. Gamma shielding will be provided by 4 in. of Pb completely surrounding the out-of-pile containments, with auxiliary shielding at the filters and other points where the radiation levels may be high. Paraffin, water, polyethylene, heavy concrete, and Masonite (Benclex 70) were considered for neutron shielding. Masonite was selected as the optimum material, based on balancing cost, fabricability, mechanical properties, hydrogen content, and fire resistance. Polyethylene will be used in place of Masonite under the overhead balcony, where space limitations place a premium on hydrogen content.

A system of gas storage tanks has been installed underground at the BGRR, to provide a means of holding up gas discharge from the loop, for decay of fission products, before discharge through filters to the reactor stack.

Specifications have been drawn up and bids received for the control and electrical power panels needed to operate the loop.

All of the analytical instrumentation, consisting of a CEC mass spectrometer, a CEC process gas chromatograph, a duPont photometer, and a TMC scintillation crystal and gamma pulse-height analyzer, is on hand and has been operated and calibrated. A mock-up of the analytical loop, including the sample-valving manifold and the diaphragm compressor that will recompress sample gas up to main loop pressure for injection back into the loop, is being built. The counters that will monitor delayed neutron and gamma levels at selected points around the loop are being calibrated.

During the design and development stages, emphasis has been maintained on the concept of the CIRC as a versatile research facility for investigating a wide variety of gas-phase reactions and

solid fuel elements of chemonuclear interest. The mechanical features and the analytical capability of the loop are carrying out this concept.

A parametric cost study for the production of ozone from oxygen in a chemonuclear process has been completed. The results indicate that a cavity reactor with U-Pd chemonuclear fuel can be designed and that a G_{O_3} of 6 or better and an ozone concentration of 0.1% or better are needed to compete with conventional ozonizers.

The nitrogen fixation is of special value in a dual-purpose power and chemical system. The power is used to generate fixed nitrogen as ammonia via electrolytic hydrogen. On an energy basis a G_{NO_2} of 6 may be sufficient to compete with conventional nitrogen fixation plants. Reactor core calculations and process designs are being made.

RADIATION CHEMICAL PROCESSING PROGRAM

This program is mainly concerned with the use of Co^{60} radiation for inducing high G -value reactions of industrial potential. An intensive study is being carried out on the radiation-induced homo- and copolymerization of ethylene, and the evaluation of the products formed. Design and economic evaluations based on the results obtained parallel the experimental effort.

Ethylene Homopolymerization

Kinetics. The experimental program for studying the polymerization of gaseous ethylene has been extended by a series of "fall-through" constant pressure experiments. The objectives of these experiments were to measure the effect of radiation intensity and pressure on the rate of polymerization, the characterization of polymer not subjected to postirradiation effects, and to obtain preliminary data on product removal.

The "fall-through" experiments were performed in a 30-in.-long vessel with a volume of 420 cc. The vessel was inserted into a lead shielding cask so that only the top 6 in. (120 cc volume) was subjected to the radiation field. Polymer was, therefore, produced in the radiation field and fell to the bottom of the vessel where it was not subjected to postirradiation. Experimental conditions ranged in pressure from 170 to 1000 atm, in temperature from 20° to 200°C, and in radiation intensity from 7.0×10^4 to 3.9×10^5 rads/hr. At a temperature of 200°C and a pressure of 680 atm, a half-power de-

pendence of the radiation intensity on rate was observed. The half-power dependence indicates a free radical mechanism and is in agreement with that previously measured at 20°C in 100-cc volume capsule experiments. The dependence of pressure on rate was determined by a series of experiments at a temperature of 200°C and a radiation intensity of 1.2×10^5 rads/hr. A pressure dependence of ≈ 2.7 was determined for the pressure range 170 to 680 atm. For the pressure range 850 to 1000 atm, a much larger effect on rate was observed. The apparent break-point, which occurred at a pressure of ≈ 800 atm, is possibly due to the increased solubility of ethylene gas in the molten polymer at these conditions.

L. KUKACKA,

R. CHAPMAN, R. HALLER, J. VARELA

Engineering Experiments. A small flow experiment has been built for the further study of the radiation-induced polymerization of ethylene. The purpose of the experiment is to study the engineering parameters in a flow system and to produce larger quantities of polymer for product characterization. The unit is designed to operate at pressures up to 2000 atm, temperatures to 250°C, and radiation intensities to 1×10^6 rads/hr. The system consists of a feed-gas compressor, flowmeter, reaction vessel, and a product separator. Interconnecting tubing is $\frac{1}{4} \times 0.083$ in. and $\frac{1}{16} \times \frac{3}{16}$ in. diameter. A 100-cc volume reaction vessel, similar to that used for static experiments, has been installed. The reaction vessel will be operated under water in a pool-type gamma facility containing $\approx 10,000$ Ci Co^{60} .

L. KUKACKA, R. CHAPMAN,

R. HALLER, J. VARELA

Design and Evaluation Studies. Preliminary design and economic studies have been made for a radiation-induced process for the polymerization of ethylene. Two processes for the conversion of ethylene to polyethylene were considered. One operates at temperatures below the melting point of the polymer ($\approx 120^\circ\text{C}$) forming solid polymer having an intermediate density, high molecular weight, and low melt index. The second process is carried out above the melting point which produces a low density polyethylene comparable to that formed in the conventional high pressure process.

The conclusions drawn from the study are as follows:

1. The cost of Co^{60} , although appreciable, is not a large factor in the conversion cost.
2. The ability to operate at high rates at pressures in the range of 680 to 1360 atm permits a

significant reduction in investment and in production cost for low density polyethylene.

3. Other grades of polyethylene may be made by the radiation process at costs comparable to those of conventional low density polyethylene.

The significance of this preliminary study is that there appears to be sufficient evidence for a continued development of radiation-induced ethylene polymerization processes.

An information meeting was held at BNL for industrial representatives on the ethylene radiation polymerization studies. An informal industrial committee was set up to evaluate the polymers formed in the flow experiments.

Polyethylene Characterization. A comprehensive study has been made on the properties of polyethylene formed by Co^{60} gamma radiation over the following range of conditions: (1) pressure from 2500 to 25,000 psi, (2) temperature from 20° to 200°C, (3) total doses from 1.0 to 5.0×10^5 rads, and (4) radiation intensity from 0.58 to 4.7×10^5 rads/hr.

The experiments were conducted in two types of reaction vessels. In the capsule type reactor the polymer resulting from the polymerization reaction remained in the radiation field for the duration of the experiment. In the fall-through type reactor the polymer fell or flowed out of the radiation field as it formed. A comparison of the structural and physical properties of polymers formed in both vessels, under the same conditions, indicated that for total doses up to 0.5 megarad, no appreciable change occurred. The functional groups for polyethylene formed by gamma radiation, including the unsaturation groups such as RCH=HCR (trans), RCH=CH_2 (vinyl), and

(vinylidene) unsaturations, were found to be in the same proportion as those in free-radical initiated high pressure polyethylenes. The methyl group content for polyethylene formed at room temperature, however, was typical of that found in commercial linear polyethylenes formed by the Phillips and Ziegler processes. The density for the unannealed polyethylene formed at reactor temperatures between 21° and 32°C remained essentially constant at 0.94 g/cc over a wide range of pressure, intensity, and dose. Careful annealing increased the density to 0.95 g/cc. Increasing reac-

Figure 11. Polymerization temperature *vs* density and methyl groups.

Figure 12. Polymerization temperature *vs* melt index.

tion temperature to 200°C resulted in a decrease in density to 0.913 g/cc, as shown in Figure 11. This results from an increase in methyl group content which is an index of the total number of both short- and long-chain branches as determined by infrared methods. A rapid change in density occurs in the softening temperature range for polyethylene. The crystalline melting point was also found to decrease with increasing temperature. The melt indices for polyethylenes formed at reaction temperatures up to the melting point of the polymer was essentially zero as shown in Figure 12. Above 126°C, the melt flow increased rapidly to a melt index value of 30 at 200°C. At a constant reaction temperature of 200°C, the melt index de-

Figure 13. Co^{60} gamma polymerization of ethylene. Intrinsic viscosity *vs* total dose.

Figure 14. Polymerization temperature and its effect on molecular weight distribution.

creases very rapidly with increasing pressure from 2500 to 14,500 psi. As the pressure increases, the molecular weight also increases resulting in a decrease in melt index.

Intrinsic viscosity, $[\eta]$, values were determined as a function of dose for polyethylenes formed at pressures ranging from 2500 to 10,000 psi. The curves shown in Figure 13 indicate a rapid initial increase in the $[\eta]$ value with dose, followed by a "leveling-off." This leveling-off indicates an approaching steady-state condition. A plot of the $[\eta]$ values obtained at the maximum doses shown in Figure 13 indicates that at these conditions the molecular weight was found to decrease rapidly with increasing temperature. Polymers formed over the entire range of conditions were found to be completely soluble in decalin at 135°C. This indicates that little or no cross-linking occurs during the reaction.

Molecular weight distribution curves were obtained for polyethylenes formed at 26°, 150°, and 200°C as shown in Figure 14. The molecular weight distribution obtained for polymer at 26°C is much greater than that obtained at the higher temperatures. This is also indicated by the ratio of the weight average molecular weight to the number average molecular weight given as $\overline{M}_w/\overline{M}_n$. The $\overline{M}_w$ value for polymer formed at 26°C is an order of magnitude greater than that obtained for polymer formed at 200°C. The wider distribution indicates a diffusion controlled termination reaction for the solid-phase polymer formed below the melting point. Above the melting point, the polymer is in the liquid phase and termination is predominately by bimolecular reaction resulting in a narrower molecular weight distribution.

P. COLOMBO, J. FONTANA

Polyethylene Radiation Stability. A study of the radiation stability of polyethylene produced by gamma radiation is under way. Radiation produced polyethylene is free of catalyst fragments as compared with commercial polyethylenes; therefore, the amount of scissions and cross-linkages induced by radiation may be different from those of commercial polyethylenes. The studies will consist primarily of the determination of the gelation point and changes in $\overline{M}_w$ and $\overline{M}_n$ values with dose. Other properties such as melting point, density, molecular structure, and molecular weight distributions will be investigated.

P. COLOMBO,

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Ethylene-SO₂ Copolymer

The Co⁶⁰ gamma-radiation-induced copolymerization of ethylene and SO₂ is being investigated. Preliminary experiments indicate that the reaction occurs both in the gas and liquid phases. Copolymers formed in the liquid phase contain equimolar concentrations of ethylene and SO₂. This was found to be independent of the initial monomer concentration. The copolymers formed in the gas phase varied in composition depending on the relative amounts of ethylene and SO₂ initially present. The experiments were prepared by pressurizing a reaction vessel containing condensed SO₂ with ethylene gas. The proportion of ethylene to SO₂ in the gas phase was varied with ethylene pressure and temperature. Copolymers containing from 1 to 99% SO₂ have been obtained.

P. COLOMBO, J. FONTANA

Survey Experiments

Ethylene-Propylene. The copolymerization reaction between ethylene and propylene in a gamma radiation field at 20°C occurs in the liquid phase. The product obtained in the gas phase at 20°C with an ethylene/propylene molar ratio of 42 was mainly ethylene homopolymer. Propylene in the gas phase seems to act as a chain transfer agent resulting in lower molecular weight polyethylene than that obtained under the same conditions in the absence of propylene. The products were identified by infrared and calorimetric methods.

Figure 15. Schematic of ammonia synthesis loop.

Monomer-Wood Polymerization. Experiments are under way for the impregnation of wood with liquid gaseous monomers which polymerize when subjected to Co^{60} gamma radiation. The first series of experiments involved woods such as pine and maple with ethylene gas at pressures to 10,000 psi. The experiments below the melting point at room temperature indicate a weight gain of the wood of 13%. Experiments are also being conducted at temperatures above the melting point up to 200°C to increase the weight loading and to improve the penetrability. P. COLOMBO, J. FONTANA

Heterogeneous Radiation Chemistry

Ammonia Synthesis. Preliminary experiments showed that the Co^{60} γ irradiation had a small but measurable effect on the synthesis of NH_3 from a H_2/N_2 mixture over a triply promoted iron oxide catalyst. There was a 5% decrease in the NH_3 synthesized at a dose rate of 3.29×10^5 rads/hr and up to 1000 psi and 500°C. To study this effect in detail, an all-stainless steel flow system has been constructed to follow the reaction thermally and in the presence of Co^{60} γ radiation. Details of the apparatus are shown in Figure 15. The pressure in the reactor is set by the tank regulator between 0 and 1000 psig and the temperature is controlled by a proportional controller to within $\pm 0.3^\circ\text{C}$, between 20° and 500°C. The gas from the reactor flows through a series of regulators to a flowmeter and into a gas chromatograph where it is analyzed for NH_3 content (0.01 to 15%) and for trace amounts of water (detection limit, 10 ppm).

The necessary detailed series of experiments on the thermal synthesis is being carried out prior to studying the effect of Co^{60} γ radiation.

A separate study is being carried out over the same catalyst on the effect of Sr^{90} β irradiation on the N_2 exchange reaction

A high vacuum apparatus has been constructed for these experiments. It consists of three sections, a volumetric gas adsorption system to measure surface areas and adsorption isotherms, a static reaction system, and a gas metering and analytical system. The rate of exchange has been followed as a function of temperature at constant pressure and an activation energy of 15.8 ± 0.4 kcal/mole has been found. A pressure dependence on the initial rate of exchange has been observed and is currently being investigated.

A reactor for the β irradiation experiments has been designed and assembled. R. DIETZ, T. HO, J. SUTHERLAND

Radiation Engineering

O. KUHL

HIGH INTENSITY RADIATION DEVELOPMENT LABORATORY (HIRDL)

Operations

All originally planned facilities at HIRDL are now operating. The irradiation cell and conveyor system are operating with a 600,000-curie Co^{60} plaque source 55 in. high and 32 in. wide.

The encapsulation of Engineering Test Reactor (ETR) sources has been completed. Of the 270 remaining cans, 156 were shipped to Oak Ridge National Laboratory unopened, and 114 were opened and encapsulated at BNL. The resulting 172 doubly encapsulated ETR sources were assigned as follows: 76 sources totaling 40,000 curies for the University of California and 92 sources of $\approx 55,000$ curies for the two shipboard irradiators.

Eight BNL standard flat sources, totaling 1156 curies, were supplied to the U.S. Department of Agriculture for the screwworm fly eradication project.

Two extracorporeal blood irradiators, each utilizing 4000 curies of Cs^{137} , were designed, constructed, and calibrated for the BNL Medical Department.

A conceptual design of a portable shipboard irradiator was completed. Two of these irradiators have been built and are currently undergoing inspection at BNL. Reviews of the design reports on the Mobile Grain Irradiator and the Bulk Grain Irradiator were made for the AEC.

Use of HIRDL Gamma Facility

The use of the facility by BNL groups and off-site researchers is summarized in Table 3.

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J. CASSIDY, G. WOODSON, F. KEUTE,
J. BYRNE, O. KUHL

RADIATION PHYSICS

Pilot Plant Studies

Pilot plant studies, using the HIRDL facility, have been initiated.

Table 3
Use of HIRDL Gamma Facility During 1965
Total irradiation time, hr

	Nuclear Engineering Dept.	Chemistry Dept.	Physics Dept.	Biology Dept.	Accelerator Dept.	Off-site users
January	478	197	962	135	—	9
February	663	180	453	51	—	2
March	1305	4	537	5	—	9
April	1067	17	481	13	—	16
May	419	929	392	183	—	4
June	1201	703	280	143	—	—
July	1533	491	390	135	—	2
August	1988	177	48	17	40	—
September	2490	389	327	21	750	2
October	1200	310	116	10	1000	11
November	936	351	139	75	550	6
December	843	—	192	55	—	38

Table 4
Dose Distribution Studies in HIRDL

Target thickness, in.	Dwell time, min	Irradiation mode	Dose, megarads		Uniformity ratio
			Min	Max	
6*	6	1 complete pass	0.780	1.40 (exp) 1.44 (calc)	1.80
6	3	1 complete pass	0.380	0.735 (exp) 0.731 (calc)	1.94
6	1	1 complete pass	0.142	0.327	2.3
3	6	1 complete pass	1.3	1.735	1.34
3	3	1 complete pass	0.618	0.84	1.35
4.25	12	2 sides of package irradiated statically at source	1.33	2.074	1.56
Heterogeneous target (cans) 4.25 in. high	12	2 sides of package irradiated statically at source	1.39	2.26	1.63
Same as above	6	1 complete pass	0.890	1.86	2.09

*Efficiency calculated for this run.

The characterization of the present HIRDL conveyor system, using both homogeneous and heterogeneous targets and the 600,000-curie plaque, is under way. The conveyor is a "feed-through" batch-type continuous irradiator. Experiments were conducted to test the effects on the dose uniformity ratio of the following parameters: the ratio of the dwell time to wipe time, and target thickness. Results of these experiments are summarized in Table 4. The efficiency of the HIRDL irradiator system was found to be 20.8%, based upon the minimum dose using a 6-in.-thick finite homogeneous unit density target and a uniformly

distributed 600,000-curie Co^{60} source plaque with 4½-in. source overlap on four sides. Analytical calculations based upon the methods given in BNL 889 (see next section) are being run in conjunction with these experiments. Thus far the experimental data and calculations agree within $\pm 3\%$.

A multipass conveyor system and a Cs^{137} source plaque have been designed and are now being fabricated for installation in the HIRDL facility. These systems will be used for pilot plant studies.

Dose distribution studies of the shipboard irradiator design indicate a uniformity ratio of 2:1 with an efficiency of 6.4% based upon minimum dose.

Table 5
Temperatures at Steady State of Sources and Arrays of Sources

Source type or name	Number of elements	Total curie content	Specific activity, Ci/g	Temperature, °C	
				Quiescent air	Natural convection
BNL Mark I Co ⁶⁰	1	5,200	80	73	55
BNL Mark I Co ⁶⁰	4 (in Al can)	20,000	80	241	—
BNL Mark I Co ⁶⁰	138 (in plaque)	600,000	80	86	72*
MPDI Co ⁶⁰	1	2,400	40	53	—
(single encapsulation)					
MPDI Co ⁶⁰	16 (in plaque)	37,000	40	—	110 to 130
Natick Co ⁶⁰	1	2,000	4	—	55
BNL Cs ¹³⁷ Cl	1	4,200	25	45	35
BNL Cs ¹³⁷ Cl	8 (in close-packed array)	33,000	25	202	166

*Air conditioning on.

Radiation Engineering Handbook

The first volume of the Radiation Engineering Handbook has been published as a separate report [BNL 889 (T-361)], entitled *Computational Methods of Gamma Irradiator Design*. This document contains the following chapters: (1) Introduction; (2) Radiation Physics – a short discussion of basic principles including interactions of gamma rays with matter, the analysis of simple source geometries and the concept of radiation dose; (3) Computational Procedures – a general approach to the problems of computational procedures in gamma irradiator design; (4) Irradiator Design – a discussion of a wide variety of general and specific irradiator design parameters; (5) Illustrative Problems – a demonstration of both analytical and empirical techniques of computational procedures; (6) References; (7) Appendices – a presentation of most of the important constants, tables, experimental data, and computer codes needed in irradiator design.

Measurement of Temperatures of Sources and Arrays of Sources

A series of surface temperature measurements at steady state of sources and arrays of sources has been made using thermocouple techniques. The results of these measurements are summarized in Table 5.

Polymethyl Methacrylate Dosimeter

When irradiated with gamma rays, commercially available polymethyl methacrylate, sold un-

Figure 16. Radiation-induced optical absorption band in 1-mm-thick UVT Lucite. Co⁶⁰ gamma dose, 3×10^6 rads.

der the trade name of UVT Lucite, develops a radiation-induced optical absorption band in the ultraviolet region of the spectrum with a peak at ≈ 275 mμ (see Figure 16). This radiation-induced band is not found in polymers produced thermally from 99.9% pure monomer.

The radiation-induced optical density of this dosimeter is a linear function of total dose over the range 5×10^3 to 5×10^6 rads (see Figure 17). The size of the dosimeter currently in use is $5 \times 12 \times 1$ mm-thick; further miniaturization is being carried out. Isochronal and isothermal bleaching studies indicate that there is negligible thermal bleaching below 80°C and that the bleaching constant is $< 0.02/\text{hr}$ at room temperature.

Figure 17. Calibration curve. Induced optical density *vs* total dose of Co⁶⁰ gamma rays in 1-mm-thick UVT Lucite.

Miniaturized Fricke Dosimeter

A miniaturized Fricke dosimeter is being developed and evaluated for use in "in-target" calibrations of absorbed dose. This system uses 0.3 cc of ferrous sulfate solution held in a polyethylene container (see Figure 18). The dosimeter is read on a standard Beckman D.U. spectrophotometer at a wavelength of 225 mμ using a dilution factor of 10 to 1. Further miniaturization studies are under way using a dosimeter volume of 0.1 cc.

Flow Chemical Dosimetry System

A flow chemical dosimeter which utilizes the Fricke dosimetry principle has been developed to measure the absorbed dose in irradiators where the target material is a fluid and is pumped past the source. This system was developed to calibrate the BNL extracorporeal blood irradiators. Its application to aviation jet fuel and flow-type chemical systems is being investigated. Figure 19 is a schematic diagram of the circulatory system. The system permits the continuous monitoring of the dose absorbed by the fluid as it is pumped through the irradiator. The ferric ion concentration is measured on a standard Beckman D.U. spectrophotometer at wavelengths of 225 and 304 mμ. These two wavelengths are used to give the system a wider range of application. The system has been evaluated for linearity of optical density *vs* irradiation time and the effect of flow rate on mixing (see Figure 20). The average dose in the irradiator is determined from the following relationship

$$D_{av} = D_T / t_R,$$

Figure 18. Comparison of size of the conventional Fricke dosimeter irradiation vessel and the miniaturized vessel.

where

- D_{av} = the average dose in irradiator,
- D_T = total dose measured in the system,
- t_R = residence time in irradiator, $= V_1 / V_2$,
- V_1 = volume of fluid in irradiator, and
- V_2 = total volume of fluid in the system.

Heat Generation in Targets

Studies of heat generation in targets in the HIRDL facility have been initiated. Figure 21 is a schematic plot of some typical data obtained in the HIRDL facility using a 600,000-curie Co⁶⁰ source and a 6-in.-thick homogeneous, unit-density target. Temperatures were measured using Chromel-Constantan thermocouples. Simultaneous temperature measurements were made at the plaque surface, on the conveyor carrier cover, and at various points throughout the target. The data in the figure are for temperatures obtained after 16 and 40 min of constant irradiation.

Figure 19. Schematic diagram of the continuous flow chemical dosimetry system.

Figure 20. Uniformity of average absorbed dose as a function of flow rate. Dosimetry solution exposed to square wave type of Co^{60} gamma radiation at a dose rate of 8.5×10^5 rads/hr.

Calorimetric Source Activity Calibration

The calibration and the initial experiments on the Mark II calorimeter have been completed. Adiabatic conditions in the calorimeter were approached by insulating the 450-lb shield with 1 in. of vermiculite surrounded by 1 in. of Styrofoam. Chromel-Constantan thermocouples, which have a high rate of change in emf with temperature, were attached to the inside and outside walls. A nanovoltmeter was used to sense the thermocouple emf to the nearest microvolt. Fifteen initial calibration runs using a specially constructed elec-

Figure 21. Thermal gradient in a phenolic target after exposure times of $t=0$, $t=16$, and $t=40$ min to the HIRDL 600,000-Ci Co^{60} source plaque.

Figure 22. Typical heater runs for calorimeter calibration. Dashed lines are least squares straight line fits; solid lines are third-degree polynomial fits.

trical heat source were made at constant power levels ranging from 30 to 125 W (see Figure 22). Two sets of thermocouple measurements for each run, time *vs* emf, were plotted and fitted to straight lines using least square approximations. Second- and third-degree polynomial fits were obtained at the same time with the IBM 7094 computer. Because of heat losses at the higher temperatures, it was observed that the second- and third-degree polynomial fits more closely approximated the

data. The slopes of the least squares straight lines were then plotted *vs* dc power for each run and were fitted to a third-degree polynomial to obtain a calibration curve (Figure 23).

BNL Standard Mark I Co^{60} sources were calibrated using this curve and a conversion factor of 15.36 W of total energy per kc of Co^{60} . Several runs were made with two Co^{60} sources and the data were fit to straight line slopes as in the calibration. It is estimated that curie content can be determined using this method with an accuracy of $\pm 2\%$. The slight curvature of each thermocouple plot, emf *vs* time, indicated that true adiabatic operation was not achieved. A mathematical computational method was devised to obtain a calibra-

Figure 23. Calorimeter calibration curve least squares third-degree polynomial fit *vs* least squares straight line heater run slopes.

Figure 24. Cooling curve for Mark II calorimeter.

tion curve of greater confidence than above by correcting for heat losses. This was done by adding the first derivative of an experimentally determined cooling curve (see Figure 24) to the first derivative of the third-degree polynomial expressions for each constant power calibration curve, and calculating a corrected slope for each constant power condition. This resulted in a revised and corrected calibration curve.

A major modification of the Mark II calorimeter has been started. True adiabatic operation will be achieved upon completion of a temperature-controlled environment chamber now being constructed. A differential temperature controller with feedback will maintain the surroundings of the calorimeter at the temperature of the exterior of the calorimeter. The concept of this modification is shown in Figure 25.

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RADIATION SOURCE DEVELOPMENT

New Sources

Specification R155-W2, Rev. 25 January 1965, was written for inactive cobalt unit-slabs clad with metallurgically bonded type 316L stainless steel.

The BNL Standard Mark II stainless steel-bonded cobalt source has been evaluated for bond quality, metallurgical defects, quality of welds, weight of cobalt, surface defects, and cobalt contamination in welds. In addition, samples have been subjected to intensive thermocycling tests between 80° to 500°C. On the basis of these tests, tentative approval for insertion into the Savannah River Plant (SRP) reactor has been granted. Three hundred samples of this source are on order with Nuclear Metals Inc., West Concord, Mass. The Mark II source is shown in Figure 26 along with its activation holder.

Metallographic examination of the bonded-type, Nb-clad, cobalt source, made by the Union Carbide electrodeposition process, showed the bond to be satisfactory after thermal cycling between 96° and 265°C for 1016 cycles.

The program to develop and evaluate binary and ternary corrosion resistant alloys of cobalt with other metals has been initiated. Preliminary evaluations were made of material fabricated from Co-Cr alloy developed at BNL for this purpose.

Figure 25. Adiabatic calorimeter (top) and adiabatic calorimeter instrumentation (bottom).

Samples of this alloy, containing 10% Cr by weight, showed corrosion resistant properties in 8 N and 16 N nitric acid which were superior to pure cobalt.

Nondestructive Testing Methods

Several nondestructive testing methods have been investigated. A thermal heat scan test method was found to be satisfactory for the evaluation of bond quality and metallurgical defects. Figure 27

shows the heat scan response of a stainless steel-clad bonded Co source specimen with known defects. In Figure 28 are shown some typical results obtained using the Mark II BNL standard Co source.

A nondestructive method of determining the weight of Co in bonded source strips is being developed. The method is based on the magnetic properties of Co and the principle of the ac electromagnet (solenoid).

FIRST ENCAPSULATION

ACTIVATION HOLDER

FINAL ASSEMBLY

Figure 26. BNL standard Mark II Co^{60} source and activation holder.

Figure 27. Heat scan test standardization with source specimen containing known defects.

Figure 28. Typical results obtained with heat scan test on BNL bonded Co^{60} source.

The solenoid apparatus was built, sample Co strips ranging in weight from 47 to 52 g were fabricated, and preliminary measurements were made. Results agreed with theory but the data displayed an excessive amount of scatter. The test specimens had not been annealed. Another set of Co strips weighing from 23 to 28.5 g were made from annealed Co. The resultant test data showed a linear relation with less scatter. However, the slope of the plotted curve did not agree with theoretically predicted results. Additional studies are in progress to obtain a proper calibration curve.

Corrosion Studies

An apparatus for conducting a corrosion study of 316 SS-clad BNL Standard Mark I and MPDI sources in an air-pool cycle was completed. In the study, specimens are heated to 125°C in moving air, then immersed in the HIRDL pool. Five cycles have been completed on two groups of specimens; one group received a radiation dose and the other, the controls, were tested unirradiated.

Corrosion test specimens were placed in the source plaques at the University of California and at HIRDL. Specimens from the University of Michigan facility will be installed soon.

Twelve ETR sources, which were returned from Israel, were examined visually and displayed no signs of corrosion. Surface stains were apparent on all specimens.

Twelve Ni specimens, of 99.9% purity, were exposed to HIRDL pool environment conditions for 1632 hr. One group of six was irradiated with Co⁶⁰ gamma rays to a dose of 6×10^8 rads; the other group served as controls. The arithmetic mean corrosion rate was found to be, for irradiated samples, 0.0028 mils/yr and for the controls, 0.0023 mils/yr.

To determine the effect of heating on the permanency of stainless steel welds, a group of specially fabricated BNL Mark I specimens were exposed to the HIRDL pool environment for 90 days. One group of welds was made using the cooling block, while the other group was fabricated without the benefit of cooling. After receiving a total dose of 8×10^7 rads, the group of welds made using the cooling block showed no signs of rust. Rust was observed on the welds made without cooling.

Source Identification Marking Methods

Since thin cladding (15 mils) is used on sources, and the trend is toward even thinner cladding,

marking methods which appreciably change the cladding thickness cannot be used.

Two marking methods are under consideration. One, the electropencil, produces a mark by formation of an electric arc which fuses and vaporizes the base metal. The other, the electrochemical method, produces a mark by electrolytically dissolving the base metal and simultaneously depositing oxide. Marking by both methods on specimens of 316L SS second encapsulations was shown to be satisfactory after exposure to the HIRDL pool environment for 90 days in a radiation field. Both methods were used to mark the frames of the HIRDL source plaque. Observations on these will be made periodically. J. WAGNER, A. OLTMANN, A. BECHT, C. DAVIS, B. SYLVESTER, E. DIVIS

Sr⁹⁰ Beta Sources

Two Sr⁹⁰ beta sources to be used for dosimetry studies and radiation chemistry experiments have been fabricated.

An 18-Ci source consisting of 36 needle-shaped elements was fabricated by the Minnesota Mining and Manufacturing Company. Each needle is doubly encapsulated with Inconel 600 and has an active length of 1.5 in. The o.d. is 0.080 in. and the wall thickness of the encapsulation is 0.010 in. The needles may be used singularly or in an array, and are designed for temperatures between -196° and 500°C at pressures to 68 atm.

The Beta Radiation Company supplied a 325-Ci Sr⁹⁰ titanate source consisting of 12 rod-shaped elements. Each rod is doubly encapsulated with Inconel 600. The over-all length is 7.5 in. with an active length of 6.5 in. The o.d. is 0.077 in. and the wall thickness of the encapsulation is 0.006 in. Design conditions for the source are 680 atm pressure at 500°C. L. KUKACKA

Exploratory Research and Development

PHOTOREACTOR DESIGN STUDIES

Several theoretical problems were under study during the year. In one, calculations were made of the performance of a tubular reactor in which the photoinitiated reaction $A \rightarrow B$ is carried out in the presence of Beer's law absorption by A and no absorption by B. At high optical densities the calculations predict the possible occurrence of a readily

Figure 29. Fraction conversion *vs* dimensionless mean residence time for the reaction $A \xrightarrow{\text{light}} B$ carried out in a continuous tubular photoreactor. Reaction tube is uniformly irradiated over its outside surface with monochromatic radiation traveling in a radial direction. Radiation is absorbed by substance A in accordance with Beer's law. τ_0 = reactor optical thickness based on feed composition.

measurable increase in conversion as the flow rate is increased from the laminar to the turbulent region (Figure 29). At low optical densities the effect can become negligibly small.

In a second study, the validity of the quasi-stationary-state approximation for intermediates in complex reaction sequences in the presence of spatially nonuniform initiation was examined. Reactor types considered included the batch reactor, the tubular reactor in laminar flow and in turbulent flow, and the continuous stirred tank reactor. Calculations were made for the simple one-center reaction $A \rightarrow B \rightarrow C$ and for a two-center regenerative mechanism. Criteria for the validity of the steady-state approximation in these circumstances have been developed.

Also, calculations have been made on a reaction in which a substance is photodissociated into two identical reactive fragments which recombine thermally. A reactant layer in the form of a slab bounded by impermeable walls was considered. In the presence of Beer's law absorption, calculations described in the previous report [BNL 900 (S-67)] showed that an increase in mean concentration of reactive fragment resulted from the introduction of rapid diffusion where there was previously none. The present calculations were concerned with intermediate rates of diffusion and were undertaken to determine the ranges of the ratio of chemical lifetime to diffusion time corresponding substantially to very fast and very slow diffusion. The problem has been solved by digital computer

in the range of rapid diffusion. Difficulties have been encountered at low diffusion rates.

Experimental study of mixing effects on chain reactions has continued. The experiments are carried out in partially illuminated stirred vessels (Figure 30). The chemical reactions involved have been the photochlorination of tetrachloroethylene in carbon tetrachloride and the direct photopolymerization of styrene. Methods of analysis of the photochlorination reaction mixture by gas chromatography and absorption spectroscopy have been worked out, and some actinometric work has been done. Initial experiments with the photochlorination in the Taylor vortex reactor disclosed an induction period comparable in duration to the maximum residence time. The induction period could be considerably reduced but not eliminated by use of more effective methods of reagent purification. Since the interpretation of data from a flow system in which an induction period was present would be very difficult, a batch reactor was selected for further work. A batch reactor was then constructed in which the inhibitor might be consumed *in situ* prior to the onset of the reaction of interest.

Following initial experiments on the direct photopolymerization of styrene, a number of refinements in design of apparatus components were introduced. While these changes were being made, further preliminary experiments were conducted. These disclosed, as expected, that when the reaction vessel was nearly fully illuminated with actinic light, no measurable effect of mixing was found. When half the vessel was illuminated an increase in rate polymerization was observed. When the temperature was increased from 30° to 35°C, the dark rate became almost comparable to the photoinitiated rate. In addition to these reaction rate studies, measurements of the light intensity incident on the reactant surface have been made, for the full spectrum of the Hg arc source, and for the beams isolated by 315, 366, and 436-m μ interference filters. The Pitts modification of the uranyl oxalate actinometer was used.

A number of exploratory experiments on the measurement of the fraction of fission fragment energy deposited in a thin fuel foil have been performed (Figure 31). The method is based on measurement of the foil temperature rise in a thermal neutron field and a comparison of this temperature rise with those induced by resistance heating of the foil with known amounts of electrical power

Figure 30. Quartz reaction vessel for the study of effects of mixing on photoinitiated reactions. Stirrer is of turbine type with hollow quartz blades containing magnetic material which permits external motivation of stirrer. Shaft and bearing surfaces are also quartz. Bearings are lubricated by reaction mixture. Four quartz baffles promote radial mixing. Top and bottom of vessel are optical flats. A parallel beam of actinic light is incident on bottom of vessel. A mask (not shown) is used to fix the fraction of the vessel which is illuminated.

Figure 31. Fission recoil energy deposition capsule. A Pd- U^{235} foil is mounted between Al terminals in an evacuated capsule. Difference thermocouple measuring junctions are located in an Al block glued to the center of the foil and in one of the terminals. Capsule is used immersed in an ice bath.

in the absence of a neutron field. More experiments must be performed before the feasibility of the method is known.

F. HILL, L. YEMIN,
D. LEE, J. EICHACKER

THE COMPTON GAMMA MONOCHROMATOR

The design of a gamma monochromator capable of utilizing kilocurie amounts of radionuclides has been completed and the instrument will be under construction shortly. The important parts of the monochromator are the radionuclide gamma

source in a shielding cask, a cylindrical metal plate scatterer, and a shielding cask for holding an object undergoing irradiation and/or a gamma detector, all located on the same circle. The energy is varied by changing the angle subtended by the arc between the source and detector. Figure 32 is a simplified drawing of the instrument as installed. The scale may be inferred from the fact that the radius is of the order of 2 m. The source cask (see Figure 33) can be rotated about a vertical axis through the source. Collimation of the gamma rays is accomplished with shielding which

Figure 32. The gamma monochromator as installed in its radiation cell. Parts of the instrument have been purposely simplified.

Figure 33. A simplification of the actual working drawings of the source cask of the monochromator.

is part of the collimator and can be rotated in the manner of a stopcock to block the gamma beam when this is desired. The detector-object cask is similar in external shape and dimensions to the source cask and can also be rotated about its vertical axis and moved along the circle. It has several access ports for photomultiplier tubes, solid-state detector diodes (with associated cryogenic equipment and preamplifiers), and objects requiring irradiation (having maximum dimensions of about 8 cm), together with an entrance collimator.

A theoretical study of the energy resolution of this instrument has been made. The energy resolution is controlled by two factors. One is the departure from ideal geometry, i.e., the fact that the source and detector or object occupy finite areas rather than points, and that the scatterer is a cylindrical shell of finite height and thickness rather than in an infinitesimally thin line. The second is the motion of the electrons in the scatterer which introduces a shift from the nominal energy of the Compton scattered photons, thus setting a maximum limit to the resolution regardless of geometric refinements.

The first effect can be calculated via a computer program. The result is illustrated, for a particular set of conditions, in Figure 34. The broadening effect due to the second cause can in principle be calculated assuming a model for the electron structure of the metal or, alternatively, the instrument can itself be used to determine the broadening due to the electron momentum distribution, and then, the distribution itself. This is to be done as follows: If the resolution function (rela-

tive intensity *vs* deviation from nominal energy) due to the deviation from ideal geometry is represented by G (Figure 34 is a typical example), that due to the characteristics of the detector is D (measured in a separate experiment using a nuclide giving the same energy of gamma as the nominal energy of the Compton scattered gamma from the instrument), and that due to electronic motion is I (the unknown), then the over-all response function R obtained from the detector is the convolution of these separate factors: $R = G * D * I$. Then, representing the Fourier integral transforms of the calculated or measured resolution functions by $\bar{G}$, $\bar{D}$, and $\bar{I}$, it follows that I is proportional to the inverse Fourier transform of $(\bar{D}\bar{G}/\bar{R})$. Expressing R , D , and G in terms of Hermite functions can be shown to be essentially equivalent to finding the Fourier integral transform of these functions. This fact has been made use of to develop computer codes which, given R , D , and G , will calculate the resolution function due to electronic motion I . It can further be shown that the electron momentum distribution function $\phi(p)$ is simply proportional to $p dI(p)/d(p)$, where p is the momentum and I is the resolution function determined above. This relation enables research on the electronic structure of metals and alloys to be carried out by using them as the scatterer in the monochromator. The experimental phase of this work will start soon. The instrument will be used for dosimetry research as well.

M. ZUCKER, A. KISTNER

Figure 34. The calculated resolution function of the present design of a monochromator under a particular set of conditions. The calculated fit with Hermite functions also provides the Fourier integral transform.

THE RECYCLE ACCELERATOR

A novel concept of a charged particle accelerator for isotope production arose out of an attempt to calculate the maximum yield of isotope per energy input that any accelerator could possibly attain. The typical reaction between a charged particle and a complex nucleus has a cross section *vs* energy which is roughly Gaussian of half width 10 to 15% of the resonant energy, and peak amplitude roughly geometrical, ≈ 1 barn. In keeping with this typical reaction cross section behavior, the following machine concept termed the recycle accelerator (illustrated schematically in Figure 35) is proposed.

A pulsed beam from an injector at energy $E_0 + \Delta E/2$ is put into a storage ring intercepted by a target of thickness $\Delta E < \Gamma/2$. After passing through the target, the beam enters an rf acceleration sta-

Figure 35. Schematic drawing of the recycle accelerator.

tion which restores ΔE to the unreacted surviving particles [the vast majority by a factor of $(\sigma_e/\sigma_n) \approx 10^9:1$, where σ_e and σ_n are typical atomic and nuclear interaction cross sections]. These then proceed in orbit until they intercept the target again. A particle recycling N times will dissipate an amount of energy $N\Delta E$ (supplied by the rf accelerating station), which for $N \approx 10$ to 100 could be comparable or even $> E_b$. It is recognized that such a machine, in the limits $N \rightarrow \infty$, $\Delta E \rightarrow 0$ (reaction rate remaining constant), $E_b \rightarrow E_r$ (where E_r is the resonant energy) would have the greatest possible efficiency, defining this to be the ratio of reaction rate R to power input P , since now the only energy being supplied to the beam goes into target dissipation. This is the only unavoidable loss since it is always in fixed proportion to the reaction rate for a given reaction. This is shown to be $R/P = (L/A)\sigma(dE/dx)^{-1}$ where L is Avogadro's number, A is the target atomic number, σ the peak value of the cross section, and dE/dx is the stopping power at the resonant energy.

The only theoretical limitation to the above scheme actually stems from the statistical nature of the Coulomb interactions in the target. While the accelerating radio-frequency gap can replace the mean energy loss in the target (ΔE), the random angular and energy deviations which cannot be compensated for will eventually limit the total

number of traversals by causing the particles to eventually strike the walls and be lost. This will occur because the repeated random perturbation of the normal betatron and synchrotron oscillations eventually results in an amplitude of oscillation too large for the beam tube. It has been shown that the successive amplitudes perform a random walk in the cross section of the beam pipe (see Figure 36). This model enabled a calculation to be made of the average number of traversals before the particle is lost (i.e., random walk terminated). Figure 37 shows the result of the calculation in the case of the betatron component of the oscillation. It should be interpreted, for example, as follows. Assume that the number of traversals was being limited by betatron type oscillations, and that a target of atomic number 100 and thickness 0.1 MeV was being bombarded by protons in a machine for which the betatron oscillation frequency is between 8 and 9. Then a reasonable estimate as to the number of traversals of the target that a particle would make before being lost is about 380. Thus the quantity $N\Delta E$ (≈ 38 MeV in this case) is liable to be comparable or even larger than the energy E_b expended in accelerating the average particle initially (≈ 16 MeV), so that more than half the theoretical maximum (R/P) efficiency would be attained. The reasonable assumption was made that the bombarding energy

Figure 36. Random walk of betatron oscillation amplitudes.

was twice the Coulomb barrier. A large fraction of the theoretical R/P will still remain even when the effect of the synchrotron oscillations is included. Thus, the recycle accelerator scheme should work in principle, although of course, practical engineering considerations and a cost analysis should be made before it can be said to be truly practical.

M. ZUCKER, B. MANOWITZ, M. STEINBERG

ION ASSOCIATION COMPLEX STUDIES

The solvation of sodium polyiodides in nitrobenzene at 25°C was studied. As sodium polyiodides are extracted from aqueous sodium iodide solutions into solutions of iodine in nitrobenzene, various numbers of water molecules are coextracted with each ion pair, depending upon the iodine content of the system. Dilute solutions of iodine in nitrobenzene give a hydration number of extracted ion pairs of about four. As the iodine content of the system increases, the hydration number increases in steps to a maximum of about eight.

L. SLATER, M. KUKK, V. ALLEN

ALPHA SOURCE CALIBRATOR EXPERIMENT

While calibrating an alpha source which developed a leak, the alpha source calibrator became contaminated. However, it was successfully decontaminated from very high levels of Po^{210} activity. The calibrator was redesigned and rebuilt so that the angle the alpha source presents to the solid-state detector can be changed while the calibrator

Figure 37. Average number of target traversals before a particle is lost, $\langle N \rangle$, divided by the betatron oscillation frequency, ν , for protons and alphas. (Assumes $E_b = 2E_c$.)

is evacuated. It is believed repeated evacuations, previously necessary to change alpha source - detector angle, contributed to the failure of an alpha source containment cover.

The calibrator was also used to observe the energies of fission fragments from thin Pd-enriched U foils. The foils were placed near a 10^8 n/sec Am-Be neutron source, containing 50 Ci (15.5 g) of Am, which was surrounded by paraffin. A low resistivity 450-mm² silicon surface barrier detector gave nearly 1000 counts/min. This figure can be increased by changing the relative positions of neutron source, foil, and detector.

Figures 38 and 39 show spectra of fission fragments from 20% enriched U foils 0.00011-in. and 0.00020-in.-thick, respectively. The total count in each spectrum was 80,644, obtained in 100 min for the thicker foil and 115 min for the thinner foil. The counts represent fission fragments leaving the foils normal, or close to normal, to the surfaces of the foils.

L. SLATER, M. KUKK, V. ALLEN

Figure 38. Analyzer spectrum of 0.00011-in.-thick Pd-enriched U foil.

Figure 39. Analyzer spectrum of 0.00020-in.-thick Pd-enriched U foil.

EFFECT OF ELECTRICAL DISCHARGE ON FLUIDIZED AND FIXED BEDS

Studies of the effect of electrical discharges on fixed beds are now essentially complete. The model previously described has been slightly modified, and agreement between experiment and theory is very good. A paper covering this portion of the program is in preparation.

Although the model adequately describes the behavior of fixed beds, it cannot be used to predict the voltage required to freeze a fluidized bed. Since there is no difference in pressure drop between a fluidized and frozen bed, there is apparently no net electrical force on the bed in the vertical direction. It is thought that the freezing occurs because of interparticle forces due to field induced dipoles, and efforts are in progress to develop a model describing this phenomenon.

Some additional data have been obtained on the effect of corona discharge on catalytic synthesis of ammonia, but reproducibility of the data is poor and the results to date are inconclusive.

Some preliminary experiments have also been performed to evaluate the use of an electrified bed as an aerosol filter. Since a frozen bed could not be maintained at gas velocities comparable to those used in electrostatic precipitators, downward flow of gas at ≈ 3 ft/sec was used. The bed consisted of 50 to 60-mesh glass beads, 1 in. in diam $\times$ 1 in. deep. Collection efficiencies for the bed with voltage applied were 97.5, 99.0, and 99.9% for aerosol particle sizes of 0.5, 0.75, and 1.1 μ , respectively.

For the bed without voltage applied, the corresponding efficiencies were 58.5, 71.8, and 82.0%. For the empty bed with voltage applied, the efficiencies were 50.0, 65.8, and 76.0%. Thus the electrified bed appears to have a significant advantage, particularly for smaller aerosol particle sizes. Further experiments are planned using larger bed particle sizes and shallower beds in order to minimize the pressure drop.

H. KATZ

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Hot Laboratory Division

L.G. STANG JR.

Isotope Research

M. HILLMAN

CHEMISTRY OF TELLURIUM

Isomer Generators

During the isomeric transition from the long-lived metastable states of Te^{127m} , Te^{129m} , and Te^{131m} to the respective relatively shorter-lived ground states, Te(VI) is reduced to Te(IV) . This phenomenon forms the basis for a possible "isomer generator" by which the ground-state nuclides could be separated at will.

When $\text{Te}^{129m}(\text{VI})$ is adsorbed on alumina and the decay allowed to occur in 3 *N* NaOH, $\text{Te}^{129g}(\text{IV})$ yields of 23% were obtained; at lower *pH*'s, yields were $\leq 19\%$. However, all such yields are far less than those obtained when growth occurs in solution. To ascertain the reasons for these differences and possibly to improve the yields, Dowex 1X10 was tried as an adsorbent. A narrow *pH* region was found in which the two oxidation states in HCl could be separated. High Cl^- concentrations enhance the separation. However, in both cases it is the Te(VI) which is less firmly bound than Te(IV) (see Figure 1).

A. WEISS

Chemical Effects of Te^{132} Decay

Discrepancies have been noted [see BNL 900 (S-67), p. 111] in various reports of the ratios of oxidation states of I^{132} resulting from the decay of Te^{132} . It has been shown that the oxidation state is not a function of solution temperature during growth. Data to date are consistent with the hypothesis that the conversion of H_6TeO_6 to TeO_4^{2-} in basic carrier solution is slow.

B. GORDON

I^{132} Yields From $\text{Te}^{132}(\text{IV})$ and $\text{Te}^{132}(\text{VI})$

Loading one series of I^{132} generators with hexavalent Te^{132} and another series with quadrivalent Te^{132} has established that (1) the initial I^{132} yield from $\text{Te}^{132}(\text{VI})$ is $\approx 3/4$ that from $\text{Te}^{132}(\text{IV})$; (2) the yields from $\text{Te}^{132}(\text{VI})$ decrease slowly and linearly

with time at the rate of 0.7 to 1.5%/day; (3) the I^{132} yield from $\text{Te}^{132}(\text{IV})$ remains constant for ≈ 1 week and then begins to decrease at about the same rate as that from $\text{Te}^{132}(\text{VI})$.

A. WEISS

CHEMISTRY OF TECHNETIUM

The chemistry of technetium and particularly of the formation of complexes involving the lower oxidation states is being investigated to characterize the properties of this artificially produced element and to provide a basis for tagging compounds with the medically important isotope Tc^{99m} .

Thus far, mild reductants, e.g., hydrazine, have failed to effect any simple reduction from the normal heptavalent state to a hexavalent state.

P. WORMINGTON

Controlled-potential coulometry and polarography have been used in an attempt to reduce pertechnetate ion to some particular known oxidation state, prior to studying complex formation. Tentatively it appears that a valence of +2 may have been achieved. Attempts to produce the green Tc(III) solution reported [SALARIA ET AL., *Anal. Chem.* 35, 979 (1963)] have been unsuccessful thus far. However, a soluble or colloidal tetravalent state having a deep beige color has been formed; on standing it becomes a brown colloidal TcO_2 or oxidizes completely to colorless TcO_4^- .

The addition of reducing and/or complexing agents, e.g., oxalate, pyridine, citric acid, and NH_4CNS , has produced new compounds having absorption spectra different from any previously reported. They are stable in air, although a N_2 blanket was used during their preparation to prevent air oxidation.

M. GREENE

REACTIONS OF TRITONS

The study was continued of the effect of spin change from reactant to product on the probability of the occurrence of a reaction induced by low-energy tritons. A refined measurement gave

Figure 1. Adsorption of Te(IV) and Te(VI) onto Dowex 1×10 from aqueous solutions of indicated pH. Each adsorption was washed with 6-column volumes of wash at the appropriate pH.

Figure 2. Excitation function of $\text{Ar}^{40}(\alpha, 2p)\text{Ar}^{42}$ reaction.

3.23 ± 0.03 for the ratio of formation cross sections, σ_g/σ_m , for the $\text{Fe}^{56}(t, n)\text{Co}^{58m, 58g}$ reactions; the corresponding spin change ratio, $\Delta I_g/\Delta I_m$, is $\frac{2}{5} = 0.4$.

Another series of experiments gave 10.2 for the ratio of formation cross sections, σ_{56}/σ_{58} , for the $\text{Fe}^{54, 56}(t, n)$ reactions, where "58" includes both metastable and ground states. The ratio of spin change for the 56-forming reaction to the average spin changes for the 58m,g-forming reactions (weighted according to the respective cross sections) is 1.5.

R. KIEFER

SPECIAL ISOTOPES

With a gas target divided into four compartments by energy-degrading foils, the $\text{Ar}^{40}(\alpha, 2p)\text{Ar}^{42}$ excitation function was measured relative to the $\text{Al}^{27}(\alpha, 3p)\text{Mg}^{28}$ monitoring reaction for which the cross section was found to be 0.0652 ± 0.0053 mb (see Figure 2).

V. WILSON

Zirconium phthalocyanine sulfate was prepared and found to undergo only little, if any, exchange with Zr and Hf ions in concentrated H_2SO_4 , indicating the possible suitability of the corresponding Hf compound as a Szilard-Chalmers target for the preparation of high specific activity Hf^{180m} .

M. HILLMAN, A. WEISS

The probable high spin of 2-hr Ir^{196} suggests that it might not be the ground state, which might decay with higher β^- energy and half-life < 2 hr. A search for this activity via $\text{Pt}^{196}(14\text{-MeV } n, p)\text{Ir}^{196}$ failed to produce sufficient activity for definite detection.

W. BISHOP

The I^{123} yield from an infinitely thick (25-mil) electrodeposited natural Sb target bombarded with 30-MeV He^3 ions was found to be $356 \mu\text{C}/\mu\text{Ah}$ at the end of bombardment. I^{124} contamination was 1.6%.

M. GREENE

Several unsuccessful attempts to produce Sc^{48m} via the $\text{V}^{51}(14\text{-MeV } n, \alpha)\text{Sc}^{48m}$ reaction indicate that if it emits 0.2 to 2-MeV gammas and has a reasonable formation cross section, its half-life is < 1 m or very long.

M. HILLMAN

OTHER NUCLEAR REACTIONS

The measured excitation function for the $\text{Ca}^{48}(\alpha, p2n)\text{Sc}^{49}$ reaction is shown in Figure 3

In trying to establish the excitation function of the $\text{Ca}^{48}(\alpha, an)\text{Ca}^{47}$ reaction in the region near the threshold energy, it was noted that when the target is covered with enough aluminum to stop all

Figure 3. Excitation function of $\text{Ca}^{48}(\alpha, p2n)\text{Sc}^{49}$ reaction.

alphas the Ca^{47} yield (from fast neutrons) is equivalent to that formed by a 2-mb alpha cross section.

B. GORDON

Triple fission to the extent described by Muga (unpublished results referred to by E.K. HYDE, *The Nuclear Properties of the Heavy Elements*, Vol. 3, p. 133, Prentice-Hall, 1964) is improbable. Evidence for this is provided by the fission yields of Ar^{39} , Ar^{31} , and Ar^{42} shown in Table 1, which also includes other yields of interest in the problem of the charge distribution in fission.

M. HILLMAN,
R. STOENNER¹

Analytical Chemistry Research

L. NEWMAN

MIXED LIGAND COMPLEXES OF PALLADIUM

Mixed complexes of Pd(II) with chloride and bromide were studied. The stepwise formation constants ($\log K$) were found to be:

$$\begin{aligned} [\text{PdCl}_3\text{Br}^{-2}][\text{Cl}^{-}]/[\text{PdCl}_4^{-2}][\text{Br}^{-}] &= 1.55 \pm 0.05, \\ [\text{PdCl}_2\text{Br}_2^{-2}][\text{Cl}^{-}]/[\text{PdCl}_3\text{Br}^{-2}][\text{Br}^{-}] &= 1.09 \pm 0.07, \\ [\text{PdClBr}_3^{-2}][\text{Cl}^{-}]/[\text{PdCl}_2\text{Br}_2^{-2}][\text{Br}^{-}] &= 0.95 \pm 0.07, \\ [\text{PdBr}_4^{-2}][\text{Cl}^{-}]/[\text{PdClBr}_3^{-2}][\text{Br}^{-}] &= 0.55 \pm 0.05. \end{aligned}$$

¹Chemistry Department.

Table 1

Fission Yields

Nuclide	Percent
Ar^{39}	$<4 \times 10^{-7}$
Ar^{41}	$<3 \times 10^{-9}$
Ar^{42}	$<3 \times 10^{-11}$
Co^{56}	$<5 \times 10^{-8}$
Kr^{76}	$<5 \times 10^{-9}$
Kr^{77}	$<4 \times 10^{-8}$
Kr^{88}	3.24 ± 0.10
Xe^{127}	$<4 \times 10^{-9}$

Table 2

Absorption of Complexes of Pd(II) With Cl^{-} and Br^{-}

Species	Absorption maxima, nm	Molar absorptivity, ϵ_{max}
PdCl_4^{-2}	279 ± 1	$11,200 \pm 50$
	222 ± 1	$33,100 \pm 100$
$\text{PdCl}_3\text{Br}^{-2}$	295 ± 5	$11,340 \pm 200$
$\text{PdCl}_2\text{Br}_2^{-2}$	300 ± 10^a	—
PdClBr_3^{-2}	310 ± 5	$11,440 \pm 200$
PdBr_4^{-2}	332 ± 1	$11,500 \pm 50$
	246 ± 1	$32,100 \pm 100$

^aPredicted theoretically from the relative absorption peaks of $\text{PdCl}_3\text{Br}^{-2}$ and PdClBr_3^{-2} .

On the basis of these constants the various spectrophotometric absorption maxima and molar absorptivities (shown in Table 2) were determined. Also on the basis of these constants the fractions of various species present at different bromide-to-chloride ratios were calculated to be:

$$\begin{aligned} \frac{3}{4} \text{PdCl}_4^{-2} + \frac{1}{4} \text{PdBr}_4^{-2} &\rightleftharpoons \text{PdCl}_3\text{Br}^{-2} & \log K &= 0.52 \\ \frac{1}{2} \text{PdCl}_4^{-2} + \frac{1}{2} \text{PdBr}_4^{-2} &\rightleftharpoons \text{PdCl}_2\text{Br}_2^{-2} & \log K &= 0.57 \\ \frac{1}{4} \text{PdCl}_4^{-2} + \frac{3}{4} \text{PdBr}_4^{-2} &\rightleftharpoons \text{PdClBr}_3^{-2} & \log K &= 0.49 \end{aligned}$$

S. SRIVASTAVA, L. NEWMAN

SYNERGISTIC EFFECTS IN SOLVENT EXTRACTION

Studies have been performed on the formation of mixed β -diketone complexes of divalent cations, e.g., MXY where HX and HY would represent two different β -diketones in an organic diluent. The extraction of UO^{+2} by acetylacetone, trifluoro-

acetylacetone, hexafluoroacetylacetone, benzoylacetone, benzoyl trifluoroacetone, dibenzoylmethane, thenoylacetone, and thenoyltrifluoroacetone was studied. In most cases, the combined chelates extracted to a greater extent than the sum of their individual extractions, which indicated formation of a mixed complex; trifluoroacetylacetone or hexafluoroacetylacetone combined with thenoyltrifluoroacetone were notable exceptions. However, further study of benzoyl trifluoroacetone plus thenoyltrifluoroacetone, acetylacetone plus dibenzoylmethane, benzoylacetone plus benzoyl trifluoroacetone, and thenoylacetone plus benzoylacetone revealed that behavior of the uranyl ion is anything but ideal; on the other hand, preliminary results indicate synergistic extraction of Cu^{+2} .

Extraction of UO_2^{+2} by dibenzoylmethane is increased by the presence of methanol, the presence of acetone, and precipitation of the complex prior to extraction, listed in order of increasing effect.

No interaction occurs between thenoyltrifluoroacetone and tributyl phosphate. No synergistic effect between thenoyltrifluoroacetone and tri-*n*-octylamine was observed in the extraction of Cu, Sc, or In; this is surprising because synergism has been observed between tributyl phosphate and tri-*n*-octylamine in the extraction of similar elements.

L. NEWMAN, P. KLOTZ

DIMETHYL SULFONE AS A SOLVENT

The over-all stability constants, β_j , of the species $\text{M}(\text{NO}_3)_j^{2-j}$, where $\text{M} = \text{Pd}, \text{Cd}$ in molten dimethyl sulfone (DMS), are shown in Table 3. The existence of DMS of nitrate complexes of lead and cadmium highly stable relative to those in aqueous solutions demonstrates the importance of the competition between hydration effects and reaction with dissolved ligands existing in such coordinating solvents as water. Cd^{+2} is more strongly hydrated in dilute aqueous solution than is Pb^{+2} and thus more difficultly reducible relative to Pb^{+2} .

C. AUERBACH, D. MCGUIRE

The dielectric constant of DMS was found to be 38.6 (5 to 10% accuracy), the solubility in water, 46 g/100 ml at $25 \pm 0.05^\circ\text{C}$, and the density, ρ , $= (1.292 - 1.16 \times 10^{-3} T) \text{ g/cm}^3$.

Over-all stability constants for palladium chloride in 1 *M* LiClO_4 -DMS in the concentration range where the degree of complex formation, n , varied from 2.9 to 4.0 were determined to be $\beta_3 = 6 \times 10^6$ and $\beta_4 = 2 \times 10^8$.

J. HASSON

Table 3

Stability Constants in Dimethylsulfone
at 125°C and Ionic Strength 2

$$\beta_j = [\text{M}(\text{NO}_3)_j^{2-j}] / [\text{M}^{+2}][\text{NO}_3^-]^j$$

	$\log \beta_1$	$\log \beta_2$	$\log \beta_3$	$\log \beta_4$
Pb	2.46 ± 0.08	3.60 ± 0.11	4.63 ± 0.10	—
Cd	2.12 ± 0.11	3.72 ± 0.14	5.19 ± 0.10	6.77 ± 0.10

CHEMILUMINESCENCE

Chemiluminescence can be produced by the electrogeneration of anion and cation radicals of many aromatic hydrocarbons at a single electrode. The light intensity produced was related to current, time, and kinetic parameters (the rate of emission is diffusion controlled) by

$$\log_{10} IF / \pi^{1/2} \varphi i_f = 1.45 (t_r / t_f) + 0.71,$$

where I = rate of light emission in moles of photons/sec, F = the Faraday, φ = the fraction of excited species undergoing radiative decay, t_f = duration of the current pulse, i_f , in the forward direction, and t_r = duration of the negative potential pulse.

S. FELDBERG, D. ROE²

ELECTROCHEMISTRY OF URANIUM

The mechanism

has been proposed for the electrochemical oxidation or reduction of several organic and inorganic species. When e_2 occurs more easily than e_1 , analyses of the polarographic and chronopotentiometric parameters as a function of the rate of step c have completely neglected the thermodynamically favorable reaction

which means that species C is virtually nonexistent and step e_2 does not occur. Computer cal-

²Massachusetts Institute of Technology.

culations indicate, and preliminary investigations verify, that the two mechanisms are indeed distinguishable.

S. FELDBERG, D. HAWLEY³

Chronopotentiometric studies showed that the reaction of U(VI) to U(IV) proceeds in aqueous acetate buffers by the second-order disproportionation of U(V) intermediates, which are complexed by the acetate ion. The rate constant, k_d , for this disproportionation was shown to be

$$k_d = k_5 K_3 [H^+] / K_w \quad (1)$$

in the following mechanism:

where $K_3 = k_3^+ / k_3^-$ and $k_d \equiv k_5 = 5.0 \times 10^2$ (liters/mol sec) at 25°C.

The addition of ethylenediaminetetraacetic acid (EDTA) to this system causes marked changes in the kinetics: The kinetics are first order with respect to U(V); the rate-determining step is H^+ -independent and [when (EDTA) > 0.01 M] EDTA-independent; EDTA complexes UO_2^{+2} weakly, UO_2^+ more strongly, UO^{+3} strongly, and UO^{+2} very strongly. Because the reaction is first order with respect to uranium, reaction (9) of the following mechanism is probably the rate-controlling step:

From chronopotentiometric data k_{10}^- is calculated to be $\approx 5.8 \text{ sec}^{-1}$. The actual disproportionation reaction, (11), is extremely rapid.

S. FELDBERG,
G. KISSEL

³University of Kansas.

DEVELOPMENT

Apart from the foregoing research, demand for analytical service required development of the following analyses: Li in Na-Li alloy with and without prior Li separation; O_2 in Li and dissolved in H_2O ; spectrography of Ta and Nb and of irradiated U; pyrosulfate fusion for Th; Ca^{+2} , Mg^{+2} , and SO_4^{-2} in sea water; controlled-potential coulometry for Fe^{+3} -U(VI) mixtures with Cu^{+2} and F⁻ present; Ag and C in metallic Na; and atomic absorption spectrophotometry for Na, K, and Mg.

Hot Laboratory Operations

P. RICHARDS

ISOTOPE PRODUCTION

The increase in the number of shipments of special isotopes made in 1965 relative to 1964 was far greater than the corresponding increase in 1964 relative to 1963. Total 1965 shipments were ap-

Figure 4. Shipments of special isotopes for 1963-1965.

Table 4
Shipments of Special Isotopes

Isotope	Number			Activity			Unit of activity
	1963 ^a	1964 ^a	1965 ^a	1963 ^a	1964 ^a	1965 ^a	
Tc ^{99m} ^b	35	303	761	3,450	37,685		mC
Mg ²⁸	199	137	154	34,450	21,350		μC
I ¹³² ^b	77	80	73	1,040	1,020		mC
Mo ⁹⁹	26	17	26	2,420	1,775		mC
K ⁴³	20	13	—	10,000	13,000		μC
Sr ^{87m} ^b	6	8	19	6	8		mC
Tc ¹³²	8	6	12	90	70		mC
I ¹³³	3	3	9	60	60		mC
(Y ⁹⁰)	2	3	3	70	45		beads ^c
Fe ⁵²	—	2	—	—	325		μC
Y ⁹⁰ ^b	5	—	1	450	—		mC
Ga ⁶⁸ ^b	5	—	1	12	—		mC
Ar ³⁸	5	d	d	210	d	d	μl ^e
Al ²⁸ ^b	2	—	—	250	—		μC
Cu ⁶⁷	1	—	1	1	—		mC
Xe ¹²⁸	1	—	—	20	—		μl ^e
I ¹²³	—	—	1	—	—	0.5	mC

^aCalendar years. ^bGenerators. ^cIndividual unirradiated beads. ^dProduction discontinued. ^eStable gas.

Table 5
Foreign Distribution of Special Isotopes^a

	Number of shipments of each isotope made				
	Tc ^{99m} ^b (6 hr)	Mo ⁹⁹ (67 hr)	I ¹³³ (21 hr)	Mg ²⁸ (21 hr)	Y ⁹⁰ Beads (unirradiated)
Canada	28	5		2	
Japan	17	1			
Argentina	12				
England			1	9	
France				32	
Switzerland					2
Australia		3			

^aHalf-life shown under each isotope.

^bGenerator.

proximately double those in 1964. The number of Tc^{99m} generators shipped in 1965 far exceeded the number of shipments of all isotopes in 1964, and was more than double the number of shipments of all isotopes made in 1963. Table 4 summarizes the production of special isotopes for the past three years, and Figure 4 illustrates the burgeoning demand for Tc^{99m} generators. It can be deduced from Figure 4 that the average amount of Tc^{99m}

loaded onto generators is increasing. Generators containing as much as 400 mC Tc^{99m} have been shipped. These larger amounts indicate that a given generator is being used to supply Tc^{99m} for more than one type of application, and that clinical use of this isotope is increasing.

Table 5 is of interest because it indicates the extent to which the use of Brookhaven-developed generators coupled with improved air transporta-

Table 6
Summary of Liquid Waste Operations

"F" Waste Released to Sewer				
	Gal	Average activity level, Ci/ml		Total activity, mCi
Dec. 26, 1964 to Dec. 25, 1965	2,820,425	4.05×10^{-12}		43.2
Dec. 26, 1963 to Dec. 25, 1964	3,376,555	1.4×10^{-11}		179.9

Waste Concentrator Operations				
			Activity in mCi	
Waste to evaporator ^a	Concentrate to drums ^a	Volume reduction	Feed	Distillate
1965 ^b	229,760	2,967	14,193	0.438
1964 ^b	189,590	2,099	14,957	3.21

"D" Waste Inventory				
	Gal start	Gal received	Gal to evaporator	Gal end
Dec. 26, 1964 to Dec. 25, 1965	66,420	217,750	226,985	57,185
Dec. 26, 1963 to Dec. 25, 1964	42,150	211,540	187,270	66,420

^aGallons.
^bNominal years (all other periods are exact years as shown).

tion have eliminated geographical limitations on the use of short-lived isotopes.

Because of the rapidly increasing medical interest in and demand for Tc^{99m} , a procedure has been developed whereby it can be produced in low-flux reactors with limited processing facilities. Multigram amounts of MoO_3 are irradiated, dissolved in NaOH , and extracted with methylethyl ketone (MEK). The MEK is evaporated to dryness, leaving carrier-free Tc^{99m} , which is taken up in saline solution ready for sterilization and administration.

Physiological saline solution has been substituted for the 0.1 N HCl previously used to elute Tc^{99m} from generators. Milking time and product volume are both reduced (and product concentration increased) by the elimination of the neutralization step and by the fact that only half as much saline is required.

Tc^{99m} production has been increased by redesigning the irradiation capsule for better heat transfer, permitting the use of larger samples containing a higher concentration of U^{235} .

Improvements in the technique [BNL 900 (S-67)] for vacuum-casting multiholed focusing

lead collimators include use of special tapered pins with heads that keep them in perfect alignment during casting even though clearances are considerably reduced; the heads also permit reuse of the pins. As a result mass production of precise 1045-hole collimators is now possible.

RADIOGRAPHY SERVICE

Demand for radiography rose sharply toward the end of the year, resulting in a total of 2453 service radiographs made, compared to 1541 made in 1964. Typical work included radiographs of a chemonuclear loop, neutron detector tubes, floors (prior to mounting heavy equipment), large tanks, a heavy-walled calorimeter, shielding plug, heat exchanger, cryostat, and a series of radiographs to study the disintegration of fuel elements at high temperature.

REMOTE CONTROL DEVELOPMENT

Construction of the Interim Alpha-Gamma Metallurgy Facility is nearing completion, and operation is expected in early 1966.

LIQUID WASTE OPERATIONS

The inventory of radioactive liquid waste was 57,185 gal at the end of the report period compared to 66,000 gal at the start. A total of 226,985 gal was processed by the waste concentrator during the year. Table 6 summarizes the liquid waste operations for the year.

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Metallurgy and Materials Science Division

D.H. GURINSKY

High-Temperature Materials Development

During 1965 the corrosion behavior of Hg, Na, and a Na-Li alloy was investigated. Details of the individual experiments are given below.

MERCURY CORROSION STUDIES

The corrosive behavior of Hg and Hg vapor at temperatures from 593° to 860°C is being studied to evaluate the long-term corrosion resistance of various materials from which a nuclear-heated turboelectric power plant may be constructed. Materials under study during the past year include pure Ta, Nb-1 Zr, and 2¼ Cr-1 Mo steel. The corrosion-inhibiting effect of ppm additions of Ti or Zr to Hg contained in 2¼ Cr-1 Mo steel systems was evaluated. The pertinent variables that appear to cause Hg stress corrosion in Nb-Zr alloys were studied.

Five natural circulation loop experiments were completed during the year. A loop of pure Ta, one of Cb-1 Zr, and three of 2¼ Cr-1 Mo steel were

tested. Operating conditions, loop characteristics, etc., are given in Table 1.

Tantalum Loop Experiment No. 137

Loop No. 137 was shut down after 19,975 hr of operation at a mean boiling and condensing temperature of 640°C and 95°C of superheat. The loop was run in a sputter-ion pumped chamber at a vacuum of $\approx 2 \times 10^{-6}$ torr. A schematic of the loop design was shown in last year's report (Figure 10a). Figure 1 shows the loop in the chamber prior to start-up. Condenser cooling was achieved by direct radiation of the condenser tubing to the water-cooled vacuum chamber walls. Mass flow rate was estimated from net boiler heat input to be $\approx \frac{1}{2}$ kg/hr, corresponding to a liquid velocity of 0.06 cm/sec (2×10^{-3} ft/sec) and a vapor velocity of 18 cm/sec (0.6 ft/sec). Boiling instabilities, i.e., temperature fluctuations of 6° to 28°C, occurred for brief periods at 11,127 and 12,610 hr after start-up. Except for these two periods, no temperature fluctuations $> \frac{1}{2}$ °C were noted during the operation of this loop. Periodic radiographs were made during shutdowns of the loop to see

Table 1

Operating Conditions for Natural Circulation Loop Experiments

Loop number	Material	Additives to Hg	Test time, hr	Mean temperature, °C		
				Boiler, condenser	Superheater	Cold leg
137	Ta	50 ppm Mg	19,975	640	735	260
143	Nb-1 Zr	None	5,712*	760	870	240
142	2¼ Cr-1 Mo steel	50 ppm Mg	4,968	593	703	270 for 3900 hr 350 for 1100 hr
144	2¼ Cr-1 Mo steel	50 ppm Mg, 3.00 g Zr	5,009	593	703	340
145	2¼ Cr-1 Mo steel	50 ppm Mg, 1.31 g Ti	4,985	593	703	360

*Rupture in loop condenser occurred at this time.

Figure 1. Ta loop in vacuum chamber.

2a

Figure 3. Loop No. 143 before operation.

2b

Figure 2. (a) Transverse section of as-received Ta tubing. (250 $\times$.) (b) Transverse section of condenser (250 $\times$) after 19,975 hr.

whether any corrosion or deposition had occurred. A radiograph made after 3126 hr of operation indicated possible voids or bubbles in the area of the "T" at the bottom of the loop. Shaking of the loop did not dislodge these voids, and subsequent radiographs all showed them. The loop had been sealed under 1 μ pressure prior to start-up.

Macroscopic examination of the inside diameter of the loop showed no visible corrosion or deposition. Microscopic examination of the "as received" tubing indicated that the inside diameter of the tubing had a roughened surface, and a number of fine, shallow grooves 15 μ in maximum depth were noted. Metallographic examination of the loop boiler superheater, condenser, and cold leg showed that each portion of the inside of the loop was similar to the "as received" standard (see Figure 2a and b). Thus, no detectable corrosion occurred during the nearly 20,000 hr this loop was operated. Analysis of the Hg inventory of the loop showed 64 μ g of Ta and 60 μ g of Mg. Thirteen mg of Mg had been added to the Hg inventory at the beginning of the experiment to insure wetting and good heat transfer.

Earlier experiments had indicated that pure Ta specimens were not corroded after 3000 hr of exposure to Hg boiling and condensing at 593°C and Hg vapor at 703°C [BNL 705 (S-60)]. In addition, the solubility of Ta was found to be <0.002 ppm in Hg at 700°C [BNL 900 (S-67)]. Thus, unalloyed Ta appears to be virtually corrosion resistant to Hg under the test conditions.

Cb-1 Zr Loop Experiment No. 143

A rupture occurred in a bend of this loop at the end superheater portion, adjacent to the condenser, after 5712 hr of normal operation.

Figure 3 shows the loop during the final stages of assembly (a schematic of the loop design was presented in last year's report as Figure 10b). After fabrication, the entire loop was annealed at 1200°C to remove all residual stresses and then was filled with 390 triple-distilled Hg and seal-welded under 1 μ vacuum. The loop boiler and condenser were operated at 760°C and the loop superheater was operated at 870°C. The stainless steel bell jar containing the loop was cooled externally by water, and a sputter-ion pump maintained a vacuum of $\approx 2 \times 10^{-8}$ torr throughout the experiment. Mass flow rate of Hg in this loop was ≈ 1 kg/hr, as estimated from the difference between operation of the loop with and without Hg. The boiler liquid velocity was 0.03 cm/sec (0.0011

ft/sec) and the vapor velocity was 36 cm/sec (1.2 ft/sec). No apparent boiling instability occurred during operation, but slight changes in temperature (1° to 6°C) in the boiler and superheater were noted in routine operation of this loop.

After the loop ruptured, the Hg remaining in it (≈ 50 g) and the Hg collected from the chamber walls were sent for chemical analysis. The loop was split longitudinally and transversely and prepared for metallographic examination. No corrosion was found in the boiler, other than a slight roughening of the boiler wall in a ring of discoloration $\frac{1}{8}$ -in. thick just below the boiler baffles. (Prior to fabrication the inside of the boiler had been polished to a mirror finish to allow detection of very small amounts of corrosion.) Figure 4a shows the discolored area, and Figure 4b shows the appearance of the smooth boiler surface about 3 cm below this discolored area.

No corrosion or deposition was noted in the superheater. However, a specimen from the superheater bend above the boiler cracked intergranularly when pressed in a vise, whereas longitudinal specimens cut from the center of the superheater and the boiler inlet bent 180° without cracking. The rupture of the loop occurred in a bend at the end of the superheater (Figure 5). This area is normally part of the superheater, and was so during the first 1990 hr of operation. Then replacement of some of the thermocouples on the superheater and addition of new Ta shielding became necessary. Subsequently the temperature in the bend area could not be brought above the 760°C boiler temperature, so that condensation occurred. Metallographic examination of the rupture area indicated that failure was completely intergranular (Figure 6a and b). No deposition was found in the loop.

The Hg vapor pressure in the loop was ≈ 1000 psi, equivalent to a hoop stress of 2500 psi. The failure of this loop was similar to that of the first (not annealed) Nb-1 Zr loop tested, No. 136 (see BNL 799, 823, and 841). Both loops ruptured intergranularly in the same loop location after long exposure to Hg and Hg vapor. These failures and subsequent tests of Cb-1 Zr alloy bend specimens in Hg and Hg vapor indicate that Nb-1 Zr is susceptible to Hg stress corrosion cracking.

Low Alloy 2½ Cr-1 Mo Steel Loop Tests

Three identical loops were fabricated from 1.25-cm-i.d. ($\frac{1}{2}$ -in. schedule 40) pipe. A schematic of the loop design was shown in Figure 7 of the previ-

Figure 4. Appearance of loop surface. *a*: Inside discolored area (1000 $\times$); *b*: in middle of boiler (1000 $\times$.)

Figure 5. Macro of failed area in Cb-1 Zr annealed loop.

Figure 6. Cross section of failed area in annealed Cb-1 Zr loop. Top, 16 $\times$; bottom, 100 $\times$.

ous annual report. The first of the three loops contained no inhibitor in the Hg; the second and third loops had a Ti and a Zr insert, respectively, in the cold leg of each loop. Fifty ppm Mg was added to the Hg inventory of each loop to promote wetting and act as a deoxidant. Mass flow in each loop was ≈ 10 kg/hr as estimated from the net heat input to the loop, i.e., heat required for operation with Hg in the loop, less the heat required for operation with the loop empty. The liquid velocity in the loops was 0.114 cm/sec (3.73×10^{-3} ft/sec) and the vapor velocity was 3.4 cm/sec (0.112 ft/sec). Each loop has completed a scheduled 5000-hr test with Hg boiling and condensing at 593°C. The maximum superheater temperature in each loop was 703°C, and the cold leg temperatures were $\approx 350^\circ\text{C}$. A portion of the boiler and all the condenser pipe in each loop were polished to a mirror finish on the inside wall to allow the depth of corrosion in these areas to be determined more accurately.

Boiling instabilities as noted by 20 to 30 and 5 to 10 psi pressure fluctuations in the Zr- and Ti-inhibited loops, respectively, occurred every 1 to 2 min. Pressure fluctuations of 10 to 15 psi occurred infrequently in the Ti-inhibited loop. Metallographic examination of each loop is in progress.

A maximum of 20 to 25 μ intergranular corrosion was found in the boiler below the nominal liquid-vapor interface and in the condenser of the uninhibited loop (No. 142). An ≈ 1 -g Fe deposit was found in the upper portion of the boiler of this loop and a 3-g deposit was found in the condenser. Virtually no boiler corrosion was found in the Ti-inhibited loop (No. 145), and no Fe deposition was found in either the boiler or condenser. A thin layer of Fe_2Ti was found in the superheater of loop No. 145, and the 1.31-g Ti insert placed in the cold leg was completely dissolved during operation. The 3.00-g Zr insert in loop No. 144 was also dissolved during operation. Visual examination of this loop's boiler and condenser showed only trace amounts of deposition. A spotty, whitish film in the lower and middle portions of the superheater was evident, and a fine, dark, powdery "dust" was also found in the middle of the superheater. Examination of all the $2\frac{1}{4}$ Cr-1 Mo steel loops will be completed and an analysis of the results given in the next report.

Stress Corrosion Cracking of Cb-1 Zr Alloys in Hg

Experiments are in progress to determine the susceptibility of Cb-1 Zr alloys to stress corrosion

cracking in Hg. Previous tests of 90° and 180° sheet bend specimens of Cb, Cb-1 Zr, and Cb-5 Zr have indicated that exposure to 760°C Hg and Hg vapor for 150 and 1000 hr results in intergranular corrosion and cracking of Cb-5 Zr alloy. Similar bend tests of Cb-1 Zr alloy were less conclusive, and pure Cb was not affected unless 5000 ppm Mg was added to the Hg. Zr in Nb-1 Zr and Nb-5 Zr alloys is apparently leached when exposed to pure Hg. Microprobe analysis of specimens exposed to Hg have not indicated Zr depletion, but analysis of the Hg in contact with Nb-1 Zr and Nb-5 Zr have definitely indicated such depletion.

Sheet tensile specimens of Nb-1 Zr alloy wetted with Hg at room temperature in Hg-HCl electrolytic cells and pulled in slow tension (0.001-in./min strain rate) failed at low stresses and underwent brittle fracture. Similar tests on sheet tensile specimens wetted thermally by being held in Hg at 593°C for 24 hr failed (at room temperature) at normal loads with no loss in ductility. Subsequent examination of specimens wetted electrolytically indicated that they had picked up hydrogen during the wetting process.

Sheet tensile specimens of Nb-1 Zr alloy wetted and 10% and then exposed to 760°C Hg for periods of up to 3 wk failed (at room temperature) under normal loads and exhibited elongations typical of well-annealed material. Apparently the exposure at 760°C was sufficient to relieve the prestrain effects and thus eliminate the residual stresses in the test specimens. Additional tests on prestrained tensile specimens in contact with Hg at 593°C are under way. Recovery or annealing of residual stresses at this temperature is not expected to occur.

Pumped Hg Loop Experiment

A Nb-1 Zr, double-diaphragm, pumped Hg loop fabricated from Nb-1 Zr alloy is in preparation. The loop is designed to boil 91 kg of Hg/hr at a temperature of 593°C. The vapor will be superheated to 703°C and passed through a 4-stage turbine simulator which will reduce the temperature to 405°C and the pressure to 30 lb/in². Vapor impingement specimens of Ta-9.5 W-2.6 Hf alloy have been inserted in the nozzle exits to determine Hg and Hg vapor corrosion and erosion resistance of this alloy and hence its suitability as a potential turbine blade material. A schematic of the loop and details of the design conditions were given in Figure 11 and Table 7 of last year's report. The

Figure 7. Appearance of inside of U-bend of T-111 after 1 wk in Hg at 650°C. (150X.)

Figure 8. Appearance of inside of U-bend of T-111 after 1 wk in Hg at 752°C. (150X.)

impingement sections in the turbine simulator are Ta-9.5 W-2.6 Hf instead of the Cb-5 V-5 Mo-1 Zr alloy noted in the earlier table.

Fabrication of the loop has been completed and the entire loop tested for leaks. All portions of the loop except the dump tank were postweld-annealed at 1200°C for 2 hr. Heaters and thermocouples are being attached to the loop and the experiment will be ready for start-up shortly.

A. FLEITMAN

LIQUID-METAL STRESS CORROSION STUDIES

Ta-8 W-2 Hf (T-111) Alloy in Hg

The attack described in previous reports of Hg on stressed Cb-1 Zr specimens was attributed primarily to a stress-sensitive, selected leaching of Zr from the alloy. It was thus of interest to determine whether "stabilized" Ta alloys would behave similarly under stress. Two strips were cut longitudinally from T-111 tubing, bent 180° in the usual fashion, and immersed in Hg for 1 wk, one specimen at 752°C and the other at 650°C. The 752°C specimen (Figure 7) showed heavy intergranular attack on the tension side, while the 650°C specimen (Figure 8) showed less severe intergranular attack but distinct evidence of cracking. Analysis of the liquid-metal samples is as follows. Sample 1 (750°C): Ta, W, and Hf were not detected (<0.2 ppm); Zr was 33 ppm. Sample 2 (650°C): Ta, W, and Hf were not detected; Zr was 21 ppm. Consequently, the Zr associated with the Hf, rather than the Hf itself, appears to be responsible for the attack. This result is rather surprising, since it suggests that Hf is insoluble or nearly so in Hg; Hf and Zr are quite similar in their alloying properties and have nearly the same solubility, on a wt % basis, in Bi at 500°C.

Unalloyed Cb in Pb-Bi

In the 1964 Annual Report, stress attack on unalloyed Cb in liquid Bi was described. Since there is some interest in using liquid Pb-Bi eutectic in contact with Cb, two U-bend specimens were immersed in Pb-Bi eutectic for 1 wk, one sample at 750°C and the other at 450°C, in the centrifuge apparatus. The 750°C specimen was severely attacked by grain boundary penetration in the high-stress area in the center of the bend, as shown in Figure 9. The attack stopped at approximately the center of the specimen, corresponding to the neutral axis in tension and compression; its depth

tapered gradually away from the area of maximum stress. The 450°C specimen was not attacked. Analysis of the liquid-metal samples was as follows: at 750°C, 8.45 ppm Cb; at 450°C, 15.3 ppm Cb. These relative amounts are not the expected ones.

J. WEEKS

ALKALI-METAL CORROSION STUDIES

Alkali metals have been proposed as coolants and working fluids in high-temperature, compact power plants utilizing the Rankine cycle. Studies are being carried out to evaluate materials to contain liquid and boiling Na in the temperature range 1000° to 1315°C. In this range only refractory metals and their alloys can be considered as suitable container materials for the Na.

The major objectives of the alkali-metal corrosion program are:

1. To study the behavior of refractory metals and their alloys in Na boiling and condensing at temperatures up to 1315°C.
2. To study corrosion and mass transfer in all liquid Na systems up to 1210°C.
3. To evaluate the relative aggressiveness of Li, Na, K, Cs, and Rb in systems boiling and condensing at temperatures up to 1210°C.
4. To investigate the effect of high-velocity Cs vapor impingement on refractory metal alloys.

Capsules, natural convection loops, and a pumped loop are being used in this work.

Earlier tests showed that unalloyed Cb (containing 600 ppm O) and Cb-10 Ta-10 W (containing 100 ppm O) were attacked intergranularly by hot-trapped Na but that, under the same conditions, Cb-1 Zr was not corroded in capsules containing Na reflux boiling at 1210°C for 5000 hr. However, localized corrosion of Cb-1 Zr was observed in capsules where up to 600 ppm O was added to the Na. No corrosion was detected after 5000 hr at 1095°C when purified Na was circulated at a flow rate of ≈ 5 g/min in a natural convection boiling loop made of Cb-1 Zr.

Capsule Tests

Capsule test No. 3, consisting of 12 Cb-base alloy capsules containing refluxing Na, was operated at 1266°C for 5000 hr in a vacuum chamber at a pressure of $< 5 \times 10^{-8}$ torr. Three of the capsules were removed and examined both metallographically and chemically. The remaining 9 capsules were then operated under the same conditions for

an additional 3000 hr. The operating conditions and the results of the examination on all 12 capsules are given in Table 2.

Aside from capsules 31 and 34, no corrosion was detected in capsule test No. 3. The detailed results on capsules 31 and 34 were given in last year's report (BNL 900). A localized deposit was found in the vapor region of capsule 29 (Y added as an insert), which penetrated the Cb-1 Zr intergranularly as shown in Figure 10. The deposit was identified by electron beam microprobe analysis as Y. No other deposits were found. Tests in which Y was placed in direct contact with Cb-1 Zr indicated that the Y will not adhere to Cb-1 Zr at temperatures $< \approx 1000^\circ\text{C}$. Therefore the Y insert in capsule 29 must have either been splashed into the vapor region during operation or adhered to the wall during the seal-welding operation.

Six capsules containing refluxing purified Na were operated at 1094°C for 10,000 hr (capsule test No. 4) to study the effect of weld contamination and postweld heat treatment on corrosion of Cb-1 Zr. The test was carried out in a chamber at a pressure of 2×10^{-6} torr. The capsules were prepared in the following manner. Duplicate capsules were welded at three levels of dry-box atmosphere contamination (purified inert gas, bottled Ar, and

Figure 9. Appearance of inner surface of U-bend specimen of Cb after 1 wk in Bi-Pb eutectic (55.5 wt % Bi). (150 $\times$.)

Table 2

Capsule Test No. 3, Operating Conditions^a and Results of Examination

Capsule No.	Test time, hr	Material	Additive, ^b ppm	Corrosion, max depth and type	Micro-hardness, ^c DPH	O ₂ in Na, ^d ppm	Net increase in O ₂ in capsule, ^e ppm	Net increase in N ₂ in capsule, ^e ppm
25	8000	Cb-1 Zr	None	None	—	11		
26	8000	Cb-1 Zr	500 Ca	None	—	12		
27	8000	Cb-1 Zr	500 Mg	None	—	9		
28	5000	Cb-1 Zr	500 Ba	None	96	<20	190	12
29	8000	Cb-1 Zr	Y	Deposit of Y in vapor region, no corrosion	97	9		
30	8000	Cb-1 Zr	150 O	None	—	11		
31	5000	Cb-1 Zr	600 O	0.025 mm, transgranular and intergranular at liquid interface	96	<25	244	18
32	8000	Cb-1 Zr	150 C	None	—	<20		
33	8000	Cb-1 Zr	600 C	None	99	18		
34	5000	Cb-10 W-10 Ta	None	0.30 mm, intergranular in vapor region; 0.80 mm, intergranular in seal-weld region	148	<140	142	6
35	8000	Cb-10 W-1 Zr-0.1 C	None	None	154	5		
36	8000	Cb-5 W-3 Zr-0.1 C	None	None	145	8		

^aTest temperature, 1266°C, chamber pressure, $<5 \times 10^{-8}$ torr.^bAll capsules were filled with cold-trapped and hot-trapped Na. Additions were made in a dry box. Oxygen added as Na₂O₂; C added as spectrographic carbon; Y not soluble and added as metal turning; Ca, Mg, and Ba added as pure metals. Capsules 34, 35, and 36 were machined from bar stock.^cPretest DPH values were Cb-1 Zr=152; Cb-10 Ta-10 W=183; Cb-10 W-1 Zr-0.1 C=210; Cb-5 W-1 Zr-0.1 C=181.^dAnalyses performed by inert gas-Hg amalgamation method. Average of 2 to 3 samples (except for #34, only 1 sample) with blank deducted. High blanks reported on samples shown by <.^eAverage of all samples for each capsule with initial O₂ or N₂ content deducted (90 ppm O₂ and 70 ppm N₂ for Cb-1 Zr; 100 ppm O₂ and 12 ppm N₂ for Cb-10 W-10 Ta).

Table 3

Capsule Test No. 4, Cb-1 Zr Analytical Results

Capsule No. ^a	PWHT ^b	Welding atmosphere	Pretest standards, ppm O		Posttest results, ppm O	
			Weld	Base material	Weld	Base material
38	No	Purified Ar	630	300	770	875
39	Yes	Purified Ar	750	250	980	(3435) ^c
42	No	800 ppm air added to bottled gas	970	720	1460	1020
43	Yes	800 ppm air added to bottled gas	810	590	2630	(2215) ^c

^aResults of samples from capsules 40 and 41 are incomplete.^bPWHT = Postweld heat-treated at 1210°C for 1 hr.^cIncluded deposit found on wall of capsule just above liquid-vapor interface.

800 ppm air was added to the dry box containing bottled Ar). One capsule from each set of duplicates was then postweld heat-treated at 1210°C for 1 hr while the other three were not. After purified Na was added to each capsule, operation at 1094°C was started.

Inert-gas fusion analyses of the capsule material taken before test (but after welding) and after test are given in Table 3. The data seem to indicate that, although the O pickup due to welding was high, operation at a pressure of 2×10^{-6} torr for 10,000 hr further increased the O level. Metallographic examination of capsules 42 and 43 showed intergranular corrosion to a depth of 0.100 mm at the liquid-vapor interface; Figure 11 is a photomicrograph of the liquid-vapor interface of capsule 42. At the liquid-vapor interface of the other four capsules, a slight (0.025-mm deep) transgranular roughening of the surface was observed; no other corrosion was detected on these capsules. The type and degree of attack seemed to be independent of weld or base material and of postweld heat treatment. Capsules 42 and 43 were attacked intergranularly probably because most of the Zr in the capsule in the region of the liquid-vapor interface was tied by O as ZrO_2 (sample of weld on capsule 43 showed ≈ 2600 ppm O). Deposits on the walls of all six capsules were identified by x-ray diffraction as ZrO_2 .

To determine the relative aggressiveness of Li, Na, K, Rb, and Cs reflux boiling in Cb-1 Zr, 12 capsules were filled, sealed, and operated under identical conditions (capsule test No. 5). Two capsules were operated without alkali metal (but were sealed under vacuum) to evaluate the effect of temperature and environment. All welds were made in an Ar-purged dry box under identical atmospheric conditions. One of each set of duplicate capsules had a longitudinal weld made with Cb-1 Zr filler wire. All the capsules were postweld heat-treated at 1210°C for 1 hr prior to being filled with alkali metal.

Each alkali metal was purified by hot trapping in contact with Zr at 650°C for 250 hr. The alkali metal was added to each capsule under vacuum, and all the capsules were sealed in an electron beam welder. The 12 capsules (2 each containing Li, Na, K, Rb, and Cs, and 2 empty) were operated for 6000 hr at 1150°C in a Viton-sealed, sputter-ion pumped vacuum chamber at a pressure of $\approx 5 \times 10^{-8}$ torr.

Metallographic examination of the capsules showed no corrosion except that the walls of the

Figure 10. Capsule No. 29 vapor region showing penetration of Cb-1 Zr grain boundaries by yttrium. (500 $\times$.)

Figure 11. Capsule No. 42, intergranular corrosion of Cb-1 Zr at liquid-vapor interface. (250 $\times$.)

Table 4

Results of Corrosion Test of High-Strength Alloy Inserts
in D-43 Capsules Containing Refluxing Na for 3000 hr at 1315°C

T, °C	Capsule No.	Material designation	Material composition, wt %	Corrosion results
1315	63	D-43	Cb-10 W-1 Zr-0.1 C	None
	64	TZM	Mo-0.5 Ti-0.06 Zr	None
	65	FS-85	Cb-28 Ta-10 W-1 Zr	Microcracks
	66	Ta-W	Ta-10 W	None
	67	T-111	Ta-8 W-2 Hf	Several pits

All capsules were heat-treated at 2200°F for 1 hr before being filled with Na.

Table 5

Capsule Test No. 11, Operating Conditions and Variables

Alkali metal:	Potassium
Container material:	D-43 (Cb-10 W-1 Zr-0.1 C)
Operating temperature:	1205°C
Hours tested:	322
Type of test:	Reflux capsules

Capsule No.	Test tabs	Nominal material	Composition, wt %
68	K-601	WC - Binderless	84.5 W-10 Ta-5.5 C
	K-801	WC - Ni Binder	88.2 W-5.8 C-6 Ni
69	K-151A	TiC-Ni Binder	58 Ti-7.5 Cb-0.5 Ta-15 C-19 Ni
	K-162B	TiC-Ni, Mo Binder	52 Ti-4.5 Cb-0.3 Ta-13 C-25 Ni-5 Mo

Table 6

Capsule Test No. 6, Alloys Tested in Refluxing Na ($T=1315^{\circ}\text{C}$)

Capsule No.	Material designation	Material composition, wt %	Material tested as
56	FS-85	Cb-28 Ta-10 W-1 Zr	Seam-weld tubing
57	T-111	Ta-8 W-2 Hf	Seamless tubing
58	D-43	Cb-10 W-1 Zr-0.1 C	Seamless tubing
59	X-34	Cb-5 W-3.5 Zr-0.1 C	Drilled rod
60	TZM	Mo-0.5 Ti-0.06 Zr	Drilled rod

capsules containing Li were slightly roughened (≈ 0.005 mm).

Capsule test No. 9, designed to evaluate several high-strength alloys in refluxing Na at 1315°C, was shut down after being in operation for 3000 hr. The operating conditions and compositions of the inserts are given in Table 4. Metallographic examination revealed no detectable corrosion on the D-43, TZM, and Ta-10 W inserts. Some surface microcracks were observed on the FS-85 sample, and slight pitting (< 0.025 mm) of the T-111 insert occurred. The D-43 capsules were not attacked.

Capsule test No. 11 consisted of two D-43 capsules containing four cermet tabs in each capsule. Two of the tabs (each of different composition) were suspended in the vapor region of each capsule while duplicates were placed in the liquid region. The boiling-condensing alkali metal in the capsules was hot-trapped K. The compositions of the tabs (supplied by Kennametal Corp.) are given in Table 5. The capsules were operated at 1205°C for 322 hr, at which time a leak occurred at the crimped section (for seal-welding) of capsule No. 68, as shown in Figure 12.

Figure 12. Capsules Nos. 68 and 69, sectioned longitudinally after test.

The Ni-bearing cermets were corroded because of dissolution of the Ni to a maximum depth of 0.025 mm; the K-151A and K-162B (TiC) alloys were attacked to the same depth, but K-801 (WC) was considerably less corroded, possibly because of its lower Ni content. The binderless WC tab (K-601) was not attacked. There was little difference between duplicate tabs located in the vapor and liquid regions.

A deposit was detected on the walls of the D-43 capsules. It consisted of two superimposed layers (Figure 13), which were identified by electron beam microprobe analysis as Fe (outer layer) and Ni (inner layer). Although the manufacturer's analysis of the cermet tabs indicated that they

were Fe-free, spectrographic analysis of the tabs indicated that Fe was present.

At the test temperature (1205°C), the results of Swisher (NASA-TN-D-2734, March 1965) indicate the following values for solubility of Fe, Ni, and Co in K containing <20 ppm O: Fe $\cong$ 1000 ppm, Ni $\cong$ 80 ppm, and Co = <5 ppm. These solubilities would explain the corrosion and precipitation found in the capsules containing the cermets with binders. In addition, Fe, Ni, Cb, and Zr in contact with each other at 1205°C can form various low-melting eutectic alloys.

Two capsule tests are currently under way and two others are ready for start-up. Test No. 6 consists of capsules of five high-strength alloys containing refluxing Na at 1315°C (Table 6). This test has been in operation for 2275 hr. The objective of capsule test No. 8 is to evaluate the relative aggressiveness of Li, Na, K, Rb, and Cs in D-43 (Cb-

Figure 13. Capsule No. 69, layer deposited in liquid region. (250X.)

Table 7

Capsule Test No. 8, Operating Conditions

Objective:

To evaluate D-43 (Cb-10 W-1 Zr-0.1 C) as container material for Li, Na, K, Cs, and Rb in separate capsules

Temperature:

1205°C

Material:

D-43 capsules, polished inside to No. 6 finish

Capsule No.	Alkali Metal*	Source
90	None	—
91	Lithium	Foote Mineral
92	Sodium	Du Pont
93	Potassium	MSAR
94	Cesium	MSAR
95	Rubidium	MSAR

*All alkali metals were purified by contacting with Zr at 650°C for 250 hr.

10 W-1 Zr-0.1 C) capsules at 1205°C (Table 7). This test has been in operation for 2050 hr.

Fifteen high-strength Cb, Mo, and Ta base alloys will be evaluated as bend specimens ($\approx 2t$, 180° bends) inserted in D-43 capsules containing refluxing Na at 1000°C. The object of this test is to determine the relative susceptibility of these alloys to cracking under residual bend stress in a Na environment.

Two Cb-1 Zr capsules containing inserts of Ta, Cb-10 W, TZM, TZC, and refluxing boiling Cs will be operated at 1000°C. The aim is to evaluate the materials used in pumped Cs loop No. 1 in a capsule test. These capsule tests (Nos. 12 and 7, respectively) are ready for start-up.

Natural Convection Loops

Loop No. 204, a small natural convection boiling loop (made from Cb-1 Zr), containing purified Na boiling at 1095°C and having a flow rate of ≈ 10 g/min (1.5 lb/hr), was operated for 8007 hr. No corrosion was detectable by metallographic examination, even on polished surfaces on which the limit of detection was 0.005 mm (2×10^{-4} in.).

Four natural convection loops have been shut down; two of them were made from Cb-1 Zr, and two were of D-43. Two loops, one Cb-1 Zr and one D-43, were run to study the resistance of these alloys to corrosion and mass transfer by liquid Na at high temperatures. The other two loops contained boiling Na in which stable boiling was

Figure 14. Schematic of pumped boiling cesium loop (revised).

achieved by means of a "bubble nucleation device" inserted below the boiler's liquid level. The operating conditions and test times for these four loops are given in Table 8. The loops have been sectioned and prepared for metallographic and chemical analysis.

Two additional high-strength alloys will be tested with boiling Na in the form of natural convection loops. A loop made from T-111 alloy (Ta-8 W-2 Hf) is ready for operation at a boiling temperature of 1315°C. An FS-85 alloy (Cb-27 Ta-10 W-1 Zr) loop has been fabricated and is ready to be filled with Na.

Pumped Sodium Loop No. 1

It has been decided to modify the pumped boiling Na loop for Cs operation. There are two primary reasons for the change in choice of working

Table 8

Operating Conditions of Natural Convection Loops Shut Down for Examination

Loop No.	Type of loop	Material	T, °C	Estimated flow rate, g/min	Test time, hr
206	Boiling	Cb-1 Zr	1204 boil, 1260 vapor	10	10,000
208	All liquid	Cb-1 Zr	1095 hot, 895 cold	50	5,000
209	All liquid	D-43	1204 hot, 1000 cold	50	5,000
210	Boiling	D-43	1260 boil, 1350 vapor	10	3,000

Table 9

Na-Li Capsule Corrosion Test No. 1^a
(Status as per radiograph, 9/8/65)

Capsule material, SS	Liquid-metal alloy	T, °C		Total cycles ^b	Total hours of operation
		Hot	Cold		
321	Li	650	500	10,208	4942
304	Li	650	500	"	"
316	Li	650	500	"	"
321	Na	650	500	9,895	4755
304	Na	650	500	"	"
316	Na	650	500	"	"
321	Na-15 at. % Li	650	500	9,782	4707
304	Na-15 at. % Li	650	500	"	"
316	Na-15 at. % Li	650	500	"	"
410	Na-15 at. % Li	650	500	"	"

^aCapsules 0.750 in. in o.d., 0.625 in. in i.d., and 8 in. long.^bEach cycle $\approx$ 15 min hot, 15 min cold.

fluids for this loop. First, compared with a Na turbine, a Cs turbine would weigh less and would have fewer stages, a lower mean blade speed, a smaller mean blade diameter, and higher quality in the last stage. Second, a Cs system would operate at lower reactor outlet and radiator temperatures than a Na system. With the present materials technology, the Na system temperatures are too high.

This change has required revision of the turbine simulator designed for Na. The head developed in the helical induction pump is considerably lower with Cs than with Na because of the much higher electrical resistivity of Cs. This limits the number of stages that can be installed in the turbine simulator to one. Two nozzle and impingement sections are installed in parallel to permit testing of two materials during each run.

The new turbine simulator section for the pumped boiling Cs loop has been fabricated and heat-treated. Both nozzles are of Cb-1 Zr while one blade is made of TZM and the other of TZC

alloy. Cs vapor will leave the boiler at 983°C, 90% quality. The vapor velocity will be $\approx$ 780 ft/sec in the nozzles, and blade impingement will be at 895°C, 86% quality. These conditions will simulate those existing in the last stage of a Cs turbine where the blade erosion due to poorest quality would be most severe.

All welding on the loop is complete, the field welds are being prepared for postweld heat treatment, and the remainder of the loop has been heat-treated. Figure 14 is a revised isometric drawing of the loop. A. ROMANO, K. HOFFMAN

SODIUM-LITHIUM CORROSION

A Na-Li alloy is of interest as a combined coolant and reactivity control for fast reactors being studied at BNL. Since one of the problems associated with the use of this liquid is its corrosiveness, a small program has been initiated to study containment materials in the 600° to 700°C maximum temperature range. Corrosion and mass transfer

are being studied initially in capsules that are temperature-cycled in a "see-saw" furnace. A description of the capsules and furnace was given in BNL 900 (S-67) (p. 138). All alkali metals are "hot-gettered" with Zr prior to filling the capsules.

Materials, test conditions, and status of the first 10 capsules are given in Table 9. The objective of this first run is to determine the relative corrosiveness of the Na-Li alloy as compared to Li and Na alone. Radiographs of all capsules after a total of 4700 hr of operation indicate no corrosion or mass transfer.

C. KLAMUT

Alloy Theory and Nature of Solids

In the metallurgy program on alloy theory and nature of solids, initial results were obtained on the liquid-Na alloy program, and the existing studies on superconductivity were expanded.

LIQUID-METAL ALLOY RESEARCH

The experimental program on liquid alloys of Na has now been under way for $\approx 1\frac{1}{2}$ years. Equipment has been constructed and preliminary data have been obtained on most of the experiments. A vacuum-inert-gas box will be used to load Na into many of the experiments, and an arm of the box will house both the electromigration and diffusion apparatus.

The effects of Li, K, Rb, Cs, Cu, Ag, Au, Cd, In, Sn, and Sb on the electron transport, mass transport, and thermodynamic properties of liquid Na are being determined. These solutes were selected because they all have filled electron cores and permit the determination of the effects of mass, size, and valence on these properties. The results of each of the experiments under way and of the theoretical calculations of the structure of liquid Na are given below.

Solubility Experiments

A precise redetermination of the liquidus curves of the nonalkali-metal solutes is being made to estimate the thermodynamic properties of these liquid alloys and to determine possible concentration ranges for use in all other phases of the program.

An apparatus built for this purpose is shown schematically in Figure 15. The Na and solute are added to a Zr crucible in an inert-gas box. Zr was selected for the crucible, since it is essentially in-

Figure 15. Schematic representation of Na solubility apparatus.

Figure 16. Device for sampling liquid Na for solubility determination. Sample chamber holds ≈ 1 cc.

Figure 17. Ag-Na liquidus, preliminary results.

soluble in Na and can act as an internal getter to maintain purity of the inert gas. Ten Wilson seals are arranged in a circle on the top of the apparatus; in the center is a stainless steel tube containing a thermocouple permanently immersed in the liquid Na. Through each Wilson seal is a $\frac{1}{8}$ -in. rod, on the end of which is a stainless steel sample (see sketch, Figure 16). The two cups making up the sampler, and the stainless steel frit were welded together in a single pass of an electron beam welder (at Elektron Standards Corp., South Windsor, Conn.).

With all the samples and rods well above the melt, the apparatus is heated in ≈ 2 psig He to the maximum temperature of the experiment for 72 hr; then the sampler is immersed in the liquid and the He overpressure is increased to 15 to 25 psig, which forces $\approx \frac{1}{2}$ cc of the liquid alloy through the filter. The sampler is then raised, the overpressure reduced to ≈ 2 psig, and the temperature lowered to a second equilibration temperature and held there 24 hr before repeating the sampling procedure. As a result, five samples are taken between the maximum temperature of the run and the melting point of the alloy by cooling the melt to each equilibration temperature, and five additional samples are taken while heating the alloy to the original temperature. The equilibration time is ≈ 22 hr at each temperature before the melt is sampled. At least two separate runs are planned on each solute.

The results obtained on the Ag-Na liquidus are compared in Figure 17 with the results (wt %) obtained at the Naval Research Laboratory (personal communication, R.R. Miller, Sept. 8, 1964).

Figure 18. Cd-Na liquidus, preliminary results.

The original alloy contained 75 g Na and 30 g Ag. The results can be approximated by the equations

$$\log_{10}(\text{ppm Ag}) = 7.248 - \frac{1493}{T(100^\circ \text{ to } 500^\circ \text{C})}, \quad (1)$$

$$\log_{10}(\text{apm}^* \text{ Ag}) = 6.449 - \frac{1439}{T(100^\circ \text{ to } 225^\circ \text{C})}. \quad (2)$$

Since the solid in equilibrium with the melt is pure Ag, one can calculate from (2) that $\Delta \bar{H} = 6583$ cal/mole Ag, and $\Delta \bar{S}' + \Delta S_i = 2.05$ cal/deg-mole. From Hultgren et al.** we find, for Ag, $\Delta H_f = 2855$ cal/mole, and $\Delta S_f = 2.31$ cal/deg-mole. Therefore, for the Ag components the partial molal enthalpy of mixing $\bar{L}_o$ is 3730 cal/mole Ag, and the excess entropy $\Delta \bar{S}'$ is -0.26 cal/deg-mole. These values are of quite reasonable magnitude.

The reason for the discrepancy between the present results and those obtained at NRL is not clear. The apparatus will be thoroughly checked for temperature gradients in the melt.

The freezing point of the alloy was found to duplicate that of the reference tank of pure Na, as determined by using the same Chromel-Alumel thermocouple. The measured emf was 5.138 mV in both cases.

*apm = atoms solute per million atoms of solution.

**R. HULTGREN et al., *Selected Values of Thermodynamic Properties of Metals and Alloys*, Wiley, New York, 1963.

The results obtained on the Cd-Na liquidus are compared in Figure 18 on an atomic percent basis with the results of C.H. Mathewson [*Z. Anorg. Chem.* **50**, 87 (1906)] and N.S. Kurnakow and A.N. Kusnetzow [*Ibid.* **52**, 173 (1907)]. At higher temperatures, the present results appear to approach the literature values; at lower temperatures they are considerably lower, possibly because of the problem of supercooling in dilute alloys inherent in the thermal arrest method used by the earlier workers. The results can be approximated by the equations

$$\log_{10}(\text{wt } \% \text{ Cd}) = 3.101 - 970/T(100^\circ \text{ to } 210^\circ \text{C}), \quad (3)$$

$$\log_{10}(\text{at. } \% \text{ Cd}) = 2.59 - 1035/T(100^\circ \text{ to } 210^\circ \text{C}). \quad (4)$$

These equations represent the equilibrium

for which the equilibrium constant K becomes

$$K = \frac{(\text{Cd})(\text{Na})}{(\text{NaCd}_2)} \simeq (\text{Cd}), \quad (6)$$

since there was excess NaCd_2 and the activity of Na can be assumed to be unity in dilute (2 at. % max) solutions. Now, at equilibrium, $\Delta F_{\text{Cd}} = RT \log (\text{Cd}) = \Delta H - T\Delta S = 0$. Thus, when $\log (\text{Cd})$ is plotted as a function of $1/T$, as in Figure 18, the straight line below 2.5 at. % Cd justifies the assumption of unit Na activity and permits the calculation of $\Delta \bar{H}$ and $\Delta \bar{S}$ from the slope and intercept of the straight line portion.

The values obtained are $\Delta \bar{H} = 4735$ cal/g-atom Cd, $\bar{L}_o = 3275$ cal/g-atom Cd, $\Delta \bar{S} = (\Delta S_f + \Delta \bar{S}^\circ) = 2.70$ cal/deg-g-atom Cd. From this latter the excess entropy can be estimated by assuming that,

Figure 19. Partial molar free energy of Cd in Na at 668° K. Solid circles from Hultgren et al.; open circles calculated from liquidus curve.

since the solid in equilibrium with the liquid is NaCd_2 , $\Delta \bar{S}_{\text{Cd}}^\circ = \Delta \bar{S} - 2\Delta S_f(\text{Cd}) = -2.22$ cal/deg-g-atom Cd.

Hultgren et al. (*op. cit.*) give values for $\Delta \bar{F}_{\text{Cd}}$ in the liquid alloy at 668° K over the composition range $X_{\text{Cd}} = 0.1$ to 1.0. By definition, at $X_{\text{Cd}} = 0$, $\Delta \bar{F}_{\text{Cd}} = \infty$. It is possible to calculate $\Delta \bar{F}_{\text{Cd}}$ at $X_{\text{Cd}} = 0.01$ and 0.02 at 668° K from BNL values and compare them with those in Hultgren et al. Figure 19 shows the results with the literature values. They lie on a reasonable extrapolation of the existing data. $\Delta \bar{F}^\circ$ at 2 at. % Cd is calculated to be +1480 cal/g-atom Cd, which is in reasonable agreement with the 1400 cal/g-atom Cd estimated by Hultgren et al. for the limiting value at infinite dilution.

Data on the In-Na liquidus are currently being obtained. J. WEEKS

Density Measurements

An apparatus for determining the densities of these Na alloys by the maximum bubble pressure method has been built and tested (see Figure 20). Purified He is bubbled through a precisely machined orifice into the liquid metal (D) at several depths, and the pressure difference between the gas pressure inside the bubble tube and that above the surface of the liquid metal is continuously recorded by the pressure sensor (B), the output going to a high-speed recorder with a rapid time response (Honeywell Electronik-19). The oil-trap (A) permits bleeding the system pressure to within the maximum safe value for the sensor (20 in. of H_2O) before the sensor is connected into the gas circuit.

Figure 20. Schematic representation of maximum bubble pressure density apparatus.

The depth of the bubble tube is read on a cathetometer, and differences in depths of immersion rather than actual known depths are used to obtain the density. The measured differences in depth must be increased by $\approx 2.8\%$ because of the increase in liquid level resulting from displacement by the bubble tube. Alloying additions to the melt can be made through the air lock (G), and the liquid can be sampled for analysis through this same port.

The pressure sensor system was designed and built by the Friez division of the Bendix Corp. The sensor itself is a flexible, stainless steel diaphragm connected to a microtransformer, the output being sent to the recorder. The pressure can be read to 0.01 in. H_2O ; full scale on the chart corresponds to 10 in. H_2O . The sensor and recorder are calibrated by comparing the chart readings with the readings from a precision manometer (Meriam-Micro-34FB2) under the same static pressure differential.

Normally 10 pressure peaks are taken, at a rate of 10 bubbles/min, at each of 10 depths for a given alloy. The density of the unknown liquid then equals

$$\rho_{\text{liquid metal}} = \frac{(P_1 - P_2)}{(d_1 - d_2)(1.028)} \times \rho_{H_2O}, \quad (7)$$

where P_1 and P_2 are the corrected chart pressure readings corresponding to two depths of the orifice, d_1 and d_2 , and ρ_{H_2O} is the density of water at the temperature at which the calibration was made.

A preliminary run with water in the tank at room temperature gave $\rho_{H_2O} = 1.0018$. Subsequently Na was added to the vessel, and no reproducible bubble patterns could be obtained. Experiments with liquid Pb-Sn alloys were then made, since the resistivities of these alloys are being investigated and they are easier to use than Na while developing the technique. For this work a glass crucible was inserted into the stainless steel apparatus to prevent attack on the steel by the Pb-Sn alloys.

Experiments with the Pb-Sn alloys indicated that the difficulties were due to erratic wetting of the tip of the bubble tube by the liquid metal. A revised technique involving maintaining the tip of the stainless steel bubble tube immersed in the liquid metal at 300° to $400^\circ C$ for several hours to promote wetting proved successful in that a regular and reproducible pattern appeared on the chart as each bubble formed and broke. Generally,

Figure 21. Density of Pb-Sn alloys at $315^\circ C$.

the bubbling was started at a fast rate, to clear any blockages, and was slowed down as the tube was pushed further into the melt. The useful pressure range (of the sensor) for Pb-Sn alloys was then 5 to 10 in. of H_2O , corresponding to a liquid depth range of 1.5 cm. This small range is the prime cause of the scatter in the results on these alloys. (The less-dense Na alloys have a far greater usable depth range.)

Three runs were made on the Pb-Sn alloys. In the first pure Sn was added, and, after its density was measured as a function of temperature, several weighed additions of Pb were made, the procedure being repeated after each addition. In the second run, Pb-Sn eutectic (38.1 wt % Pb) was added to the system, and further Sn additions were made to change the composition down to 33.8 wt % Pb. The third run covered the composition range 15 to 28 wt % Pb. All runs were made at $411 \pm 2^\circ C$.

The results obtained are compared in Figure 21 with the earlier work of Fisher and Phillips [*Trans. AIME* 200, 2060 (1954)] on this system. The results on pure Sn are inexplicably high, but the remainder are generally in good agreement. The compositions of the alloys indicated in Figure 21 are estimated from these weighed additions. Some additions failed to go into the crucible, as indicated by both the cathetometer and chart readings; these additions were not included in estimating concentrations. Samples of the liquid were taken and have been sent to the analyst.

Sodium has again been added to the apparatus, and, by prewetting the tip, satisfactory bubble patterns have been obtained. J. WEEKS, B. FROST,*

P. ADAMS

*On leave from A.E.R.E., Harwell, England.

Figure 22. Schematic representation of liquid metal resistivity cell.

Resistivity Experiments

The technique developed for the measurement of resistivity in the constant-pressure phase of the program is a conventional 4-probe potentiometric method. The resistivity is determined by measuring the potential difference developed by a known current in a capillary tube of known dimensions containing the liquid specimen. Figure 22 is a schematic diagram of the resistivity cell.

Many liquid binary alloy systems have been studied during the past eight years by means of the magnetic induction technique. Numerous anomalies have been observed in the resistivity variations with composition, and these have been related to the phase diagrams and to component compositions. To confirm the validity of using the magnetic induction technique for resistivity determinations, and also to check the performance of the potentiometric method apparatus, a detailed examination of one of these binary alloys was undertaken. Use of a glass cell allowed measurements to be made on the Pb-Sn system up to 530°C (see Figure 23). Subject to a complete thermocouple calibration, the temperature coefficients of all the alloys appear to decrease slightly with temperature. The experimental errors are of the order of 0.2%.

The variation of resistivity with composition at 500°C is shown in Figure 24, together with the data obtained by using the magnetic induction technique [A. ROLL AND G. FEES, *Z. Metallk.* 51, 1

(1960)]. The resistivity variations observed by Roll and Fees are several times larger than their estimated experimental error (1%). No such anomalies are observed in the present work. This is shown more clearly in Figure 25, in which the resistivity difference from the straight line joining the pure metal values is plotted. The present work indicates a completely smooth variation of resistivity with composition. These observations cast doubt on anything other than the major resistivity trends determined by the magnetic induction method. Work on this system will be completed in the next period.

A resistivity cell has been constructed for the examination of liquid Na alloys. The capillaries are fabricated from a high-density polycrystalline alumina (Lucalox) which is compatible with Na up to the boiling point. Two capillaries are incorporated in the cell to enable the specimen homogeneity to be verified. The specimen temperature is measured by two tantalum-sheathed Pt-13% Rh-Pt thermocouples. The outer containment of the cell is 347 stainless steel.

The resistivity variation of Na as a function of temperature is being measured. This work will be followed by an investigation of the variation of resistivity with composition of a series of Na alloys.

P. ADAMS

Thermoelectric Power

Preliminary measurements have been made of the absolute thermoelectric powers of solid and liquid Na, K, Rb, and Cs. The apparatus used consisted essentially of a long, thin column of alkali metal with Cu counterelectrodes in electrical contact with it at two well-separated points. The alkali metal was held in a Pyrex, quartz, or Lucalox tube, and a thin foil of Mo or Ta separated it from the Cu.

Figure 23. Temperature dependence of electrical resistivity of Pb-Sn alloys.

During one experiment the temperature of one junction was maintained constant while that of the other was varied over a wide range. The temperature of each junction was measured by a thermocouple Ag-soldered to the foil at the same point as the Cu wire. A plot of the thermal emf of the Cu-alkali-metal system $E_{\text{Cu,M}}$ as a function of temperature was then made and the thermoelectric power $(dE/dT)_{\text{Cu,M}}$ obtained directly from the plot. This is a temporary measure, since the thermocouples used in the experiments have not yet been calibrated, although they are known to agree within $\pm 1\%$ with the tabulated values at 100°C . Final values for the thermoelectric power will be obtained by fitting an equation to the data by the least-squares method and having the computer print out the slope at suitable temperature intervals.

Experiments were first carried out on a sample of commercial Na (analysis showed that a similar sample contained 0.2% Si), and the results are given in Figure 26. It can be seen that, despite the impurity, the present data fall within the range covered by previously reported measurements. The upper temperature limit of this experiment was limited by the epoxy resin used to hold the Mo foils in place.

Figure 24. Composition dependence of electrical resistivity of Pb-Sn alloys at 500°C .

Figure 25. Resistivity deviations from weighted values of pure components of Pb-Sn alloys at 500°C .

Measurements are now in progress on very pure Na, and the results, so far for the solid only, are proving to be more negative by $\approx 1 \mu\text{V}/^\circ\text{C}$ than those for the commercial Na.

Results for K, Cs, and Rb were obtained with use of a second cell in which the Mo foil was fused directly into the wall of a quartz capillary tube. The upper temperature limit of this cell was set by the attack of the alkali metals on quartz. The values obtained for K are shown in Figure 26; again the agreement with previous work is quite good. The result obtained for Cs is shown in Figure 27. Note that the absolute thermoelectric power of Cs

Figure 26. Thermoelectric power of liquid Na and K.

Figure 27. Thermoelectric power of liquid Cs.

is positive immediately above the melting point, whereas it is negative for Na, K, and Rb; it becomes negative for Cs in the region of 300°C.

Results are not shown for Rb because measurements were made over only a very limited temperature range on each side of the melting point and the specimen was heavily oxidized. Despite the oxidation, the agreement with published values was reasonable; the change in the absolute thermoelectric power on melting was from $\approx -8.5 \mu\text{V}/^\circ\text{C}$ in the solid to $\approx -6.0 \mu\text{V}/^\circ\text{C}$ in the liquid.

An apparatus is being assembled to measure the thermoelectric power of Li, and more work is obviously required on the other alkali metals before their absolute thermoelectric powers can be said to be well established.

The work on pure Na mentioned earlier forms the first stage of a measurement on an alloy sys-

tem. A diagram of the apparatus used is shown in Figure 28. The quantity of Na in the cell is known, and, when the measurements on the pure metal are completed, a known amount of solute will be added. Mixing will take place in the wide part of the cell at the bottom, and a range of compositions will be covered by successive additions of solute.

P. KENDALL

Radial Density Function for Liquid Sodium as a Function of Distance (in Å)

One of the most interesting questions to be answered about a liquid is, what is its structure? It is easy to characterize the structure of a solid as a periodic array of atoms, but what is the equivalent model for a liquid? Machine calculations are being run which will answer this and other questions about a liquid metal. A long-range oscillatory potential which should approximate Na was chosen; and the program, worked out in conjunction with Rahman of Argonne National Laboratory, should give the detailed position, velocity, and acceleration of Na atoms as a function of time. Initial results are now emerging. In Figure 29 the calculated density of pairs of atoms is plotted as a function of distance. It can be seen that the radial density function does approximate the neutron data for Na. An attempt is being made to determine more detailed properties of the model liquid and thus gain further insight into the nature of liquid metals.

A. PASKIN

Electromigration and Diffusion Experiments

A vacuum dry box for the handling of liquid and solid Na in an inert atmosphere has been constructed and is being tested. An apparatus has been built for the measurement of electromigration and diffusion rates of various solutes in liquid Na. This will be attached to a specially designed evacuation lock of the dry box to permit handling the Na before and after experimentation without exposure to air.

Liquid Bi experiments are being continued until the dry box and accessory equipment can be made operational for Na experimentation. Electromigration and diffusion measurements have been completed for Ag and are now being made for Cd and In in liquid Bi. It is planned to perform these measurements for the same series of solutes in liquid Bi that will be studied in liquid Na to provide a basis for comparison of solvent as well as solute.

Figure 28. Thermoelectric power apparatus for liquid alkali-metal alloys.

Figure 29. Radial distribution function for liquid Na.

In Figure 30 the final Ag-Bi diffusion data, plotted as $\log D$ vs reciprocal temperature, are given. Also shown is the temperature dependence of the electric mobility, U , of Ag in Bi. From these data the effective valence, Z^0 , for Ag in Bi can be calculated by using a modified Nernst-Einstein equation,

$$U = Z^0 e D / kT, \quad (8)$$

where e is the electron change, k the Boltzmann constant, and T the temperature. Values of effective valence are plotted against reciprocal temperature in the lower portion of Figure 30.

Electromigration measurements for Cd and In in liquid Bi have been performed in a manner similar to that for the Ag-Bi measurements. However, retaining Cd in the Bi in vacuum proved to be difficult because of appreciable vaporization of the Cd, especially at temperatures $>400^\circ\text{C}$. This problem was partially solved by heating the alloy with a positive pressure exerted by a He atmosphere in the apparatus, which was then evacuated for only a short time prior to the filling of the capillaries. Thus experiments with Bi-Cd were made at temperatures up to 500°C with only a small loss of Cd.

Preliminary data showing the temperature dependence of the electric mobilities of Cd and In in Bi are plotted in Figure 31; the temperature dependence of the Bi-Ag data is given for compari-

Figure 30. Chemical diffusivity and calculated effective valence of Ag in Bi.

Figure 31. Electromigration results on Cd and In in liquid Bi.

son. Both Cd and In in Bi migrate toward the cathode, as did Ag, but with a mobility more than four times that of Ag. The mobility values found for Cd and In were surprisingly similar, and, although individual straight lines have been drawn through the data points for each alloy, perhaps a single line may be warranted. A few additional runs may be performed to clarify this. In addition, the diffusion coefficients of Cd and In in liquid Bi are being determined so that effective valences may be calculated. S. EPSTEIN, J. RUTHERFORD

Figure 32. The temperature dependence of $H_{c3}/H_c \propto \kappa$ in the 2-fluid model and from experiment for strong- and weak-coupling superconductors. For convenience the experimental values of κ (in arbitrary units) are normalized to the value of $\kappa(\alpha = \frac{1}{2})$ at $t = 0.4$.

SUPERCONDUCTIVITY PROGRAM

During the past year, the basic research and the development effort in high-field superconductivity were combined into a single coordinated program. This work is now housed in the Metallurgy building to provide constant interplay between the development and the research groups. The Nuclear Engineering, Physics, and Accelerator Departments are supporting the cooperative program.

Theory

Various theoretical problems have been solved in support of the experimental superconductivity program. To explain the detailed temperature dependence of the Ginzburg-Landau parameter κ in a range of materials, the 2-fluid model was generalized. In particular, it was extended to cover the cases of strong and weak coupling superconductors; this extension was straightforward. The generalized 2-fluid model was adjusted to fit the detailed temperature behavior of the critical magnetic field. Calculation of the temperature dependence of κ for a series of strong and weak coupling materials yielded the correct detailed differences between the two types of superconductors as

Figure 33. The energy gap parameter as a function of film thickness (a).

shown in Figure 32. Because of the interest at BNL in thin films, a microscopic BCS type of calculation was made for very thin films. For films of the order of 30 $\text{\AA}$ or less, the gap parameter or the critical temperature was found to rise sharply with decreasing film size, as shown in Figure 33. The detailed rise in temperature shows quantum effects, which probably are not observable, as well as an average increase in temperature, which should be observable. Future experiments should decide whether this effect plays an important role in very thin films.

A. PASKIN

Experiment

The thin film program has proceeded with both tunneling and resistance measurements. Tunneling measurements in magnetic fields led to the discovery of high transition temperatures in thin Al films. These temperatures were then studied by measuring the resistance along the films. The behavior of T_c as a function of film thickness was studied and a superimposed layer model was suggested to explain the results. The suggestion of Ginzburg (Lebedev Institute of Physics, Moscow) of an enhanced interaction at a superconductor-dielectric interface was also employed in this model. In Figure 34 a plot of T_c vs film thickness is shown. The heavy line is a theoretical curve computed from the layered-film model.

Superconductivity has also been discovered in W films, and measurements have been made to establish some of their superconducting properties. Transition temperatures as high as 4.2° K have been found in these films, compared with <0.01° K in the bulk. In Figure 35 some representative transitions are shown. The critical field at $\approx 1^\circ \text{K}$ was

Figure 34. Data showing the dependence of T_c on thickness. $\circ$ - Films deposited in filament evaporator. $\square$ - Films made in electron beam evaporator.

found to be $>35,000$ Oe. These measurements are now being extended to $>80,000$ Oe.

In both Al and W films the critical fields have been measured as a function of the angle between the field and the plane of the film. From the ratio of $H_{\parallel}$ to $H_{\perp}$, information about the film properties and mean free path have been obtained.

Tunneling measurements into bulk Nb have been started in cooperation with Prof. D.H. Douglass of the University of Chicago, and these preliminary measurements are being extended at both Brookhaven and Chicago.

The resistivity and tunneling measurements will be extended into the 80,000 Oe region in the immediate future. The program will also be extended to new techniques of making ultrathin films and also phonon spectra in superconducting alloys.

M. STRONGIN, O. KAMMERER

X-ray and electron microscopy investigations were carried out to determine film structure. Transition temperatures were found to be a function of the amount of x-ray line broadening, which has been analyzed as broadening due to small particle size and strain. A small-angle scattering measurement was made on one amorphous film. One very broad, diffuse line was noted. A few particle-size measurements were also made by electron microscopy. The results agreed reasonably well with the x-ray particle-size determinations.

The effect of oxygen on these films is now being investigated. Preliminary experiments have shown that the transition temperature is lowered as the oxygen content is decreased. In addition, the effect

Figure 35. The temperature dependence of the transition in W films ≈ 2000 Å thick.

	"Apparent" x-ray particle size, Å	Preparation	Film resistance, Ω
A.	180	annealed at 600°C	360.
B.	130	evaporated	340.
C.	310	annealed at 600°C	96.
D.	150	sputtered	4.5
E.	100	evaporated	220.
F.	100	evaporated	88.
G.	≈ 20	evaporated	180.
H.	80	sputtered	70.
I.	≈ 20	evaporated	320.

The evaporated films were ≈ 2.5 cm long and 0.3 cm wide. The sputtered films were ≈ 1.5 cm wide. Some films sputtered on Teflon were found to have essentially the same temperatures as films evaporated or sputtered on Al_2O_3 , glass, or quartz substrates. The ac measuring current in almost all cases was $< 2 \mu\text{A}$ peak to peak. Insert shows the variation in T_c with the apparent x-ray particle size.

of other phases such as the β tungsten structure will be considered.

O. KAMMERER

Measurements of ac susceptibility have been applied to the study of surface currents in superconductors from just below H_{c2} to H_{c3} . Critical surface currents have been obtained from measurements of the transition dc field as a function of ac amplitude in Pb-Bi alloys in which the Ginzburg-Landau parameter, κ , ranges from 1 to 5. The critical current values were compared with those predicted by J.G. Park from a calculation based on Ginzburg-Landau theory and found to be in reasonable agreement. Structure in the susceptibility vs steady-field curves has been observed and explained in terms of sample end effects.

A model relating ac susceptibility, surface critical currents, and bulk magnetization curves

has been developed. This model is capable of explaining the present work as well as previous susceptibility data taken in this laboratory.

B. BERTMAN, M. STRONGIN

In addition to the work described above and in last year's report, studies on irreversible superconductivity have been initiated. The results of the first experiments show that the properties of remnant flux in Nb, Pb, Bi, Sb in Sn, and Pb in In systems cannot be explained by assuming the existence of either thermal barriers to flux motion or thermally activated pinning sites. Experiments in which remnant flux changes with temperature were measured in zero applied magnetic field do not show any of the expected kinetic behavior associated with a thermal barrier model. The temperature dependence was found to vary with a thermodynamic property of the system, i.e., H_c in type I and borderline type II systems and H_{c2} in the stronger type II systems. These data, measurements of the magnetization behavior, and changes in remnant flux in the presence of transport currents can be explained by postulating the existence of a surface barrier in the form of a shielding current which is responsible for the properties of irreversible superconductors. The model predicts "training" effects, the critical current *vs* field variation with defect concentration, and an upper limit

for the equilibrium current-carrying capacity for any system. It is well known that, when magnetization curves of irreversible superconductors are determined, the magnetic moment changes along a diamagnetic whenever the field is reversed. The value of the moment associated with the diamagnetic depends on that of the external field at which reversal is induced. In addition, at a given field, the value of the moment associated with the diamagnetic is smaller in minor hysteresis loops than in the major hysteresis loop. These effects are shown in the magnetization curve of 1.5% Bi in Pb given in Figure 36. The curve with single arrowheads was taken by cooling the normal material to 4.2°K, increasing the external field to 525 Oe, and then decreasing it to zero. The curve with double arrows was obtained by first cooling the normal material to 4.2°K, and then increasing the external field to ≈ 1000 Oe before removing the applied field (not shown). After the external field had been decreased to zero it was again increased and decreased (Figure 36, 2nd cycle). The third cycle was taken by increasing the field from 0 to 525 Oe before decreasing it to zero.

The diamagnetic observed during field reversal demonstrates the existence of a surface shielding current proportional in magnitude to the magnetic moment of the diamagnetic. An immediate consequence of the difference between minor and major hysteresis loops is the observation that the shielding current is not a unique function of the external field, but increases when fields exceeding H_{c2} are applied and removed before reapplying fields lower than H_{c2} . Thus the "training" effect follows directly from the magnetization behavior and should occur in all irreversible superconductors.

It is worth noting that if the current associated with the field change were not on the surface, the slope of the magnetization curve during field reversal operations would not be completely diamagnetic. In all the systems studied to date no measurable difference could be found between the initial slope during field reversal and the diamagnetic obtained below H_{c1} from the first magnetization measurements.

A second consequence of this explanation follows from the known observation that cold working increases hysteresis, i.e., lowers the reverse magnetization curve relative to the forward curve. This in turn requires the diamagnetic at each field point to increase with cold work. Therefore, the maximum obtainable shielding current at each

Figure 36. Minor and major hysteresis loops in 1.5% Bi in Pb at 4.2°K.

value of the external field increases with cold working. In the limit of complete irreversibility the trapped field corresponds to H_{c2} . The maximum shielding current therefore occurs when $\Delta M = H_{c2}/4\pi$.

It has been possible to show that when an arbitrary amount of trapped flux is introduced at a given temperature (T_1) through a minor hysteresis loop, any small transport current in zero field will expel some of the flux. If the same quantity of flux is put in at a higher temperature and the sample is subsequently cooled to T_1 , small transport currents do not expel flux. Thus, the maximum shielding current for a given sample is not uniquely determined by the magnitude of trapped flux, but depends on how the flux was introduced.

A high-sensitivity Foner magnetometer is being modified by the addition of a superconducting magnet so that magnetization measurements can be taken on higher field superconductors. These measurements will be made over a wider range of temperatures. The equipment will be used to support the studies on irreversible superconductivity and to help initiate a program to measure magnetization curves of thin films.

D. SCHWEITZER,
B. BERTMAN

Development

Considerable progress has been made in the development of superconducting devices during the past year. A high-field solenoid with a conical bore has recently been built and is being tested. This solenoid will be used in the high energy physics program and is expected to produce a maximum field of 130 kG. A quadrupole magnet employing mutually perpendicular current sheets has been tested recently. The results indicate that field gradients considerably higher than those now in use can be obtained by using superconductors. Work is in progress on a "split pair" solenoid designed to produce 100 kG and intended for use in neutron polarization studies.

Studies of the characteristics of "flux jumps" in Nb_3Sn magnets at reduced temperatures indicate that the performance of solenoids made from this material can be greatly improved by operating them below the lambda point. This is of particular interest because solenoids made from NbZr have been found to operate at the same or lower currents at temperatures $< 4.2^\circ\text{K}$.

Magnetoresistance probes have been developed which have a linear response to field above 3 kG. When coupled to the appropriate circuitry they

allow a direct readout of field to be displayed on a digital voltmeter.

A technique has been developed for measuring magnetic fields in very small volumes. This method employs bismuth fibres and allows an accurate determination of the field to be made in a region with dimensions of only a few thousandths of an inch.

W. SAMPSON

Radiation Effects

Studies on radiation effects in the Metallurgy Division during 1965 included effects on both the mechanical and microstructural properties of Fe. In addition a study of annealing for the prevention of radiation embrittlement of steels has been initiated.

THE EFFECT OF IRRADIATION ON THE DEFORMATION OF IRON

Studies made here have shown that fast neutron irradiation ($> 1\text{ MeV}$) increases the yield and flow stresses of iron and inhibits the strain hardening process. Furthermore, in iron containing $> \approx 10$ ppm interstitials, a low-temperature embrittlement effect is induced above a threshold exposure of 10^{18} nvt.* Recovery of this brittle effect begins at annealing temperatures of 250° to 300°C , whereas recovery of the general radiation hardening requires an annealing temperature of 400°C .

STRESS RELAXATION AND SINGLE-CRYSTAL STUDIES

In order to understand these mechanical property effects, experiments designed to study the behavior of dislocations are being performed. The variation of dislocation velocity with applied stress has been studied at different temperatures before and after irradiation by using a stress relaxation technique originally proposed by Noble and Hull [*Acta Met.* 12, 1089 (1964)].

The experimentally determined relation between dislocation velocity and stress is given by $v = (\tau/\tau_0)^m$ where τ_0 is a constant proportionality factor. This can be rewritten as

*Fission threshold of U_{238} . The exposures were calculated from Cs_{137} activity by using a cross section of 0.31 barns and a fission yield of 6.2%.

Figure 37. The variation of m with temperature in iron before and after fast neutron irradiation.

Figure 38. The effects of temperature and irradiation on the activation volume for plastic flow in single and polycrystalline iron.

$$m = \frac{\ln v}{\ln \tau},$$

and, if the mobile dislocation density is assumed constant during the stress change,

$$m = \frac{\ln \dot{\epsilon}}{\ln \tau},$$

since $\dot{\epsilon} = \phi \rho b v$, where $\dot{\epsilon}$ is the plastic strain rate, ρ the dislocation density, b the slip vector, and ϕ a constant. Noble and Hull have shown that, using

Figure 39. The effects of temperature and irradiation on the activation energy for plastic flow in iron.

the above assumption, the slope of the log of the relaxation stress σ vs the log of the relaxation time is equal to $1/(1-m)$. Accordingly, we have determined values of m for Ferrovac iron before and after irradiation; the results are shown in Figure 37. Furthermore, from rate theory the activation volume V^* is given by

$$V^* = kT \left(\frac{\partial \ln v}{\partial \tau^*} \right)_T,$$

where τ^* is the effective stress at the barrier. From the preceding discussion it can be seen that $V^* = m k T / \tau$. From this equation the activation volume for the rate-controlling deformation process in iron before and after irradiation was calculated (see Figure 38). Finally, the activation energy, ΔH , is given by $\Delta H = V^* T \partial \tau^* / \partial T$; the energies thus calculated are shown in Figure 39. The m and V^* values for irradiated iron below the brittle transition temperature of 130°K were obtained by a delayed-yield technique and can be seen to be a continuous extrapolation of the ductile range data. (Point A in Figures 37 and 38 was obtained in pre-yield relaxation and point B after the delayed yield was initiated.)

These results indicate that a mechanism change may be induced by irradiation at 300°K. Recent data on unirradiated iron with a different impurity level suggest that this 300°K effect is due to dislocation interactions with impurities or point defects. Below 300°K there is no mechanism

change induced by irradiation except, perhaps, a small frictional effect. The transition from ductile to brittle behavior appears to be strictly one of initiating a sufficient dislocation flux to maintain the applied strain rate in the specimen.

The apparent difficulty in producing sufficient dislocation flux in irradiated iron at low temperatures could be due to an agglomeration of defects on preferred planes. This in turn could block or inhibit the operation of one or more of the three known slip systems in iron. Accordingly, a single-crystal study is being carried out on iron crystals oriented for single slip on each of the three slip systems to determine the temperature dependence of the shear stress of each slip from 77° to 300°K, and the effect of irradiation on this dependence. Initial results show that slip is reduced to widely spaced, heavy bands, and that the ability to cross-slip has been considerably reduced. A rounded Gilman-Johnston type of yield drop is induced in ductile crystals by irradiation. Furthermore, only the (112) {111} system has shown any ductility below 130°K. Ramaswami [*J. Appl. Phys.* **36**, 2569 (1965)] has proposed that cross-slip and twinning are dependent stress-relief mechanisms; in last year's report it was shown that twinning is considerably reduced by irradiation. Since the predominant stress-relieving deformation made in iron below 130°K is twinning, its inhibition by a high concentration of radiation defects may be the major cause of embrittlement. The single-crystal work should clarify this point.

A series of experiments in which iron samples will be irradiated and tested at subzero temperatures is under way. If the embrittlement phenomenon is caused by an interstitial impurity-radiation defect interaction, an irradiation test conducted at temperatures below which interstitials can move should prove this. One experiment has just been completed in which Ferrovac iron tensile specimens were irradiated at -70°C to an exposure of 2×10^{18} nvt ($E > 1.45$ MeV) neutrons and stored at -196°C until tested. The ductile to brittle transition at 130°K (-145°C) produced by irradiation at +70°C to the same exposure level was not observed. Therefore defects that are mobile above -70°C must interact to produce the observed embrittlement in iron. S. McRICKARD, J. CHOW

Reverse Strain Relaxation Studies

In last year's report, data on the reverse strain relaxation of Ferrovac E iron, decarburized iron,

Figure 40. Decay of reverse strain rate for unirradiated Ferrovac E iron.

carburized Ferrovac E iron (to 700 ppm C) and Ferrovac E iron irradiated to 2×10^{18} nvt were presented and analyzed with use of the general creep equation $\dot{\gamma}_R = A t_R^{(n-1)}$, where $\dot{\gamma}_R$ is the reverse strain rate, t_R is the reverse relaxation time, and A and n are constants.

Figure 40 presents data on unirradiated Ferrovac E iron for various holding times in the deformed state prior to load release, plotted as $\log \dot{\gamma}_R$ vs $\log t_R$. The 5-, 10-, and 20-min curves are parallel and can be separated into two linear segments, stage I, < 1 min, and stage II, > 2 min. The holding time effect appears only as a change in the parameter A . This indicates that the reverse flow mechanisms are independent of holding time and that the absolute magnitude of the reverse rate, as represented by A , is controlled by the forward processes occurring during the holding period; this provides a means of separating forward and reverse processes. The data for a holding time of 40 min show an initial stage in which $n > 0$ and then a final stage which becomes parallel to stage II of the shorter holding time curves. For the 60-min curve, n is still positive in the initial stage, but is lower than in the case of the 40-min curve. Again the final stage is parallel to the latter part of the other curves. After a 120-min delay, the curve shows three stages.

By means of a similar series of tests with decarburized iron, carburized iron with 700 ppm C,

Figure 41. Effect of 4-hr irradiation ($\approx 5 \times 10^{15}$ nvt > 1.45 MeV) on the decay of reverse strain rate of Ferrovac E iron.

and Ferrovac E iron irradiated to 2×10^{18} nvt, stage I can be associated with reverse dislocation tangling, stage II with immobilization by accumulation of a carbon atmosphere, and the positive n of stage I with unpinning of dislocations pinned during forward relaxation. The value of A is related to the movement of dislocations through the lattice into tangled configurations, redistribution of the tangles, and pinning by carbon or dislocation interactions during forward relaxation. In iron irradiated to 2×10^{18} nvt, there appeared to be less tangling or carbon pinning in the forward direction, since more mobile dislocations were present for reverse relaxation.

During the past year Ferrovac E iron specimens irradiated to lower exposures were studied to establish the sensitivity of the technique in detecting the transition stages between unirradiated and irradiated iron.

Reverse relaxation data for 4-hr and 3-day irradiations are presented in Figures 41 and 42 respectively. A summary of the n values for the holding times studied is given in Figure 43, together with data for Ferrovac E iron in the unirradiated condition and irradiated to 2×10^{18} nvt.

For the 4-hr exposure ($\approx 5 \times 10^{15}$ nvt) Figure 43 shows that, for holding times up to ≈ 15 min, the n values for stage I are approximately equal to those of the unirradiated iron. For longer holding times, the n values become positive, but the rise is not as rapid as in the unirradiated iron, which in-

dicates a decreased tendency for forward pinning. In addition, for the longer holding times a second stage appears of the same order as that of the unirradiated iron.

For the 3-day exposure ($\approx 1 \times 10^{17}$ nvt), the first stage was logarithmic ($n=0$), with a slightly positive deviation appearing only after a prolonged holding time of 120 min. The n values for the second stage did not vary with holding time and were more positive than those for the second stage in unirradiated iron (less carbon effect).

For the 2×10^{18} nvt exposure, both stages I and II were logarithmic.

A composite of the A values obtained for the different irradiation levels is shown in Figure 44. The results are as follows. (1) The initial reverse relaxation rate increases as the exposure increases. Apparently, as the irradiation level increases, dislocation motion becomes restricted to specific systems, which results in a configuration more like those characteristic of low stacking fault energy metals. More dislocations, then, are free to contribute to reverse flow, and the result is a higher rate. Interaction in the reverse direction is also impeded as n in stage I approaches zero. (2) The rate of change of A with holding time decreases with increasing exposure. This indicates an increased resistance to dislocation motion

Figure 42. Effect of 3-day irradiation ($\approx 1 \times 10^{17}$ nvt > 145 MeV) on the decay of reverse strain rate of Ferrovac E iron.

through an irradiated lattice. A level of 2×10^{18} nvt is sufficient to prevent the time-dependent redistribution of dislocations characteristic of the unirradiated material. (3) Forward pinning, as represented by a decrease in A and $n_I > 0$, is inhibited by increasing exposure and is not present in the 2×10^{18} nvt samples. The tendency for pinning to decrease can be a result either of the removal of carbon from solution or of restriction of dislocation interlocking in tangled networks by inhibition of cross glide. Further work on irradiated decarburized iron is being carried out to clarify this point. It is interesting to note that the highest reverse relaxation rate was found in the 1×10^{17} nvt samples after a holding time of 120 min. The migration and redistribution of dislocations took place relatively slowly but, because of the lack of pinning, continued for a prolonged period.

Tests were also made on 1×10^{17} and 2×10^{18} nvt samples annealed at 400°C for 2 hr. The results were essentially the same as those for the unirradiated iron, which indicates that the findings are truly effects of irradiation.

On the basis of the data obtained to date, the following conclusions are offered.

1. Since stage II is associated with carbon pinning, it would appear that removal of carbon from solution takes place progressively as the exposure increases, and is completed at 2×10^{18} nvt.

2. An exposure of 1×10^{17} is sufficient to hinder cross glide and reverse tangling, as indicated by a

Figure 43. Summary curves for values of n for Ferrovac E iron irradiated to various exposures. Grain size, 0.040 mm.

Figure 44. Summary curves for values of A for Ferrovac E iron irradiated to various exposures. Grain size, 0.040 mm.

logarithmic first stage ($n_I = 0$) and the decreased rate of change of A with holding time.

3. On the assumption that a decrease in A is caused by pinning and that $n_I > 0$ represents unpinning, a decreased tendency for pinning is found with increasing exposure.

4. From the magnitudes of the A values, the initial dislocation configurations (low holding time) show a decreased tendency towards forming tangled networks as the exposure increases.

5. The ease of movement of dislocations to change the configuration during the forward relaxation decreases with increasing exposure.

6. The results demonstrate that the technique is sensitive to the effects of irradiation levels as low as 5×10^{15} nvt.

Further studies will be made of the effects of the irradiation level, annealing, and temperature.

J. CHOW, R. ROSENBERG

ELECTRON MICROSCOPE STUDY OF CARBON PRECIPITATION IN IRRADIATED IRON

Wagenblast and Damask [*J. Phys. Chem. Solids* 23, 221 (1962)] and Hull and Mogford [*Phil. Mag.* 6, 535 (1961)] have reported that the rate of carbon precipitation in iron is enhanced after neutron irradiation. Wagenblast and Damask found that the kinetics of carbon disappearance from solid solution were quite different when the iron was irradiated at $\approx -100^\circ\text{C}$ from those following irradiation at reactor ambient temperature (57°C), and therefore concluded that the mode of disappearance was different. They attributed the carbon disappearance in the low-temperature irradi-

Figure 45. Precipitation in iron containing 90 ppm C after irradiation to an exposure of $\approx 5 \times 10^{15}$ nvt and aging for 1 hr at 100°C. (40,000 $\times$.)

Figure 46. Precipitation in unirradiated iron (90 ppm C) after aging 1 hr at 150°C. (40,000 $\times$.)

ated iron to carbon-vacancy trapping. Both groups attributed the enhancement of precipitation in iron irradiated at reactor ambient temperature to precipitation at the increased number of sites created by irradiation. If this is so, the rate of carbon disappearance and the number of precipitates should increase with exposure. However, both groups of investigators reported that the effect observed saturated after a very low exposure ($\approx 5 \times 10^{15}$ nvt).

The objectives of the present investigation are to study the morphology of carbon precipitation in irradiated iron and to learn more about the saturation effect. Zone-refined irons with carbon contents ranging from ≈ 10 to 150 ppm are being studied.

Prior to irradiation or aging the iron foils were quenched from 720°C. The irradiated foils were exposed for 4 hr in a water-cooled hole of the BGRR at a temperature of $\approx 30^\circ\text{C}$ and an integrated flux of $\approx 5 \times 10^{15}$ nvt.

Figures 45, 46, and 47 illustrate the results for iron containing 90 ppm carbon. Figure 45 shows precipitation in irradiated iron aged for 1 hr at 100°C. The precipitation is general throughout the lattice. The precipitates appear to be flat discs and some appear to be loops. No precipitation was

Figure 47. Precipitation in irradiated iron (90 ppm C) (exposed to $\approx 5 \times 10^{15}$ nvt) after aging 1 hr at 150°C. (40,000 $\times$.)

found in aging unirradiated iron at a temperature as high as 130°C. Precipitation was first found in unirradiated iron aged at 140°C. Figure 46 and Figure 47 respectively show unirradiated and irradiated iron aged at 150°C. Note the differences in morphology of precipitation in the irradiated iron; there is an area denuded of precipitation adjacent to grain boundaries and dislocations.

J. KELSCH, J. CHOW, A. DAMASK

INHIBITION OF EMBRITTLEMENT OF IRRADIATED STEELS BY PERIODIC ANNEALING

Considerable evidence exists in the literature to indicate that radiation-induced defects become more complex and more stable with increasing exposure. In a review of the irradiation effect on face-centered cubic metals, Makin* pointed out that a higher annealing temperature for recovery and higher activation energy for dissociation are required for heavily irradiated copper. Bryner** suggested that in iron irradiated to exposures up to 2×10^{18} nvt ($E > 1.45$ MeV) the defects when annealed can easily escape from the lattice without forming visible loops, whereas the defects in the more highly irradiated iron agglomerate into visible loops when annealed. These visible loops persist and affect the mechanical properties. Chow et al.† showed that in pure iron there was an exposure threshold for embrittlement at low temperature. This threshold is between 8×10^{17} and 2×10^{18} nvt. Berggren†† reported a break upward at $\approx 4 \times 10^{18}$ nvt in the shift in the impact transition temperature vs exposure curve for a steel. This evidence strongly suggests that embrittlement can be inhibited by frequent annealing to prevent the defects from agglomerating into the more stable complex defects. Simple defects may anneal out at low temperatures and the material may never become embrittled. If these concepts can be applied to large structures it may be possible to avoid an unsafe operating condition.

A program is under way to study the effect of periodic annealing on the impact transition of ir-

radiated steels. A carbon steel (A212) and a low alloy steel (A302) are included in the study. The experimental work consists of annealing the impact specimens after every exposure increment of $\approx 1 \times 10^{18}$ nvt. Isochronal anneals of 4 hr at 200°, 300°, and 350°C are being studied to determine the lowest temperature that will prevent embrittlement. A set of impact specimens will be tested after total exposures of 3×10^{18} , 5×10^{18} , and 8×10^{18} nvt. These data will be compared with the shift in impact transition of specimens simultaneously exposed but not intermittently annealed. The program was started in July 1965. Significant results on exposures to 5×10^{18} nvt should be obtained by January 1966, and definitive results by June 1966.

J. CHOW, S. McRICKARD

ELECTRON MICROSCOPIC STUDY OF THE EFFECTS OF FAST NEUTRON IRRADIATION ON THE MECHANICAL PROPERTIES OF IRON

In conjunction with the study of the effects of fast neutron irradiation on the mechanical properties of iron and iron alloys, the effects on the microstructure of these materials are being investigated by electron-transmission microscopy. The purpose of this investigation is to observe the radiation-induced defects which change the properties or to observe their effects on the dislocation substructures generated by plastic deformation after irradiation. It is hoped that correlation of such observations with the results of mechanical property determinations will lead to an understanding of the mechanism by which fast neutron irradiation changes the mechanical properties of iron.

Observation of Radiation Defects

Results of the investigations described in last year's report suggested that the concentrations of loop-forming defects were limited by the carbon contents and that the loop-forming defect might consist of carbon atoms combined with individual or clustered Frenkel defects (vacancies or interstitial iron atoms).

During the past year the possible relationship between the loop-forming defects and interstitial impurity atoms were explored. Postirradiation heat treatments were carried out on 2×10^{20} nvt-irradiated specimens of iron containing 0.030 wt % carbon, produced by remelting Ferrovac E and adding carbon. The area of spots and loops was observed to increase to a maximum after 2 hr at

*Makin, M. J., Radiation damage in face-centered cubic metals and alloys, *Proc. AIME Symp. Radiation Effects, Asheville, N.C., Sept. 1965* (in press).

**Bryner, J. S., A study of neutron irradiation damage in iron by electron-transmission microscopy, *Acta Met.*, in press.

†Chow, J. G. Y., McRickard, S. B., and Gurinsky, D. H., *ASTM Spec. Tech. Publ.* 341, 46 (1963).

††Berggren, R. G., Neutron irradiation effects in steels, *Iron Steel Inst. (London) Spec. Rept.* 69 (1961).

Figure 48. Spots and loops in remelted iron irradiated to 2×10^{20} nvt and heated at 400°C for 2 hr in a vacuum. *a*: Heated as 0.012-in.-thick disk; *b*: heated as electron-transparent foil

400°C and then to decrease. The maximum loop area was approximately equal to that previously observed in the purified iron irradiated to 2×10^{20} nvt. This result showed that the previous relationship between the carbon contents and the concentrations of loop-forming defects was fortuitous, and suggested strongly that the loop-forming defects do not contain carbon atoms. Because the purified iron was lower in nitrogen and oxygen than the as-received Ferrovac E, it still seemed possible that the loop-forming defects might contain nitrogen or oxygen.

A method of exploring this possibility was devised which eliminated the time and expense of preparing and irradiating irons richer in nitrogen or oxygen than the as-received Ferrovac E. It had been observed that the Ferrovac E and the purified iron had the same grain size, both had been slowly cooled after the preirradiation anneal, and in both the 2×10^{20} nvt irradiation under identical conditions had increased the room-temperature yield stress by $\approx 17,000$ psi. Thus both irons as irradiated appeared to contain the same concentration of radiation defects capable of affecting the yield stress, and the yield stress change appeared to be independent of the concentration of loop-forming defects. These observations suggested that the purified iron at least must contain invisible

radiation defects other than the loop-forming defects, which are also capable of affecting the yield stress but do not form visible aggregates during postirradiation heating. It seemed possible that the nonloop-forming defects might be the Frenkel defects or defect clusters which combine with an interstitial impurity atom to form a loop-forming defect. If so, they might be converted to loop-forming defects by adding the right interstitial impurity atom to the 2×10^{20} nvt-irradiated purified iron and thus increasing the maximum loop area produced by postirradiation heat treatment of this material

To test the effect of adding oxygen, specimens of unirradiated and 2×10^{20} nvt-irradiated purified iron were electrolytically thinned to electron transparency and then heated in a vacuum at 400°C for periods ranging from $\frac{1}{2}$ to 4 hr. These treatments were intended to allow oxygen from the oxide surface layer left by the thinning and rinsing to diffuse into the iron film, which was of the order of 10^{-5} in. thick. A monolayer of oxygen on each side should correspond to a bulk concentration of ≈ 0.1 at. % oxygen. After being heated, the specimens were given a very short electrolytic polish to remove any surface effects and then examined by electron transmission microscopy. The unirradiated specimens contained relatively massive particles of a second phase which was not present in specimens of the same material similarly heated in bulk before thinning. These particles were mostly at grain boundaries. In addition to

similar massive particles, the irradiated specimens contained dark spots in approximately the same concentration observed previously in specimens of the same irradiated material similarly heated in bulk. However, the spots in the film-heated material were larger. The spot area per unit volume increased with time to a maximum after ≈ 2 hr and then decreased. The maximum value was much greater than that observed in bulk-heated specimens of the same material and was approximately equal to that previously observed in 2×10^{20} nvt-irradiated as-received Ferrovac E heated in bulk. The increased spot area resulting from thinning before heat treatment can be readily seen by comparing Figures 48a and 48b. Similar experiments on as-received, 1×10^{19} nvt-irradiated, and 2×10^{20} nvt-irradiated Ferrovac E specimens thinned to electron transparency before heat treatment produced approximately the same maximum spot area per unit volume as in bulk-heated specimens. In a specimen of 2×10^{20} nvt-irradiated Ferrovac E containing 0.03 wt % carbon, thinned to transparency and then heated in a vacuum for 2 hr, some areas contained a greater spot area per unit volume than was found in bulk-heated specimens, but others did not. In no area was the spot area greater than the maximum observed in the 2×10^{20} nvt-irradiated as-received Ferrovac E. Whether the specimens were slowly or rapidly cooled after being heated at 400°C had no effect on the spot areas in these oxygen-treated specimens.

The results of this set of experiments indicate that the 2×10^{20} nvt-irradiated purified iron contained, in addition to the loop-forming defects, other radiation defects which could be converted to loop-forming defects by adding oxygen. The total concentration of loop-forming defects and "convertible" defects appeared to be the same in both the as-received and the purified Ferrovac E after the 2×10^{20} nvt irradiation, which indicated that this total concentration was limited by the integrated flux rather than by the impurity level. It is not clear whether the loop-forming defects in the as-received Ferrovac E were formed during irradiation or during postirradiation heat treatment. Since an appreciable fraction of the maximum loop area per unit volume observed in the 2×10^{20} nvt-irradiated purified iron was present in the as-irradiated condition, some loop-forming defects must have formed during the irradiation. Since the increase in yield strength produced by the 2×10^{20} nvt irradiation was the same in these

materials, it would appear that the unaggregated loop-forming defects and the "convertible" defects have the same effect on the ambient temperature yield stress. The erratic effects of adding oxygen to the iron containing 0.03 wt % carbon in increasing spot area were probably due to the fact that most of the carbon was segregated in widely dispersed carbides. In the vicinity of these carbides, the carbon content of the iron may have been high enough to prevent penetration by the surface oxygen.

In a specimen of 2×10^{20} nvt-irradiated purified iron that had been electrolytically thinned to 0.002 in., heated in a vacuum at 400° for 2 hr, and then thinned to electron transparency, the spot area per unit volume was equal to that of a specimen of the same material similarly heated in bulk, and no second phase was detected. This result indicated that the surface oxygen did not diffuse to a depth of 0.001 in. during the heat treatment. On the basis of these experiments the diffusion coefficient of oxygen in iron at 400°C appears to lie between 7×10^{-13} cm²/sec and 5×10^{-10} cm²/sec.

To test the effect of adding nitrogen, specimens of unirradiated and 2×10^{20} nvt-irradiated vacuum-remelted Ferrovac E were electrolytically thinned to 0.002 in., heated in ammonia at 400°C for 2 hr, furnace-cooled, and then thinned to electron transparency. The unirradiated specimen contained relatively large particles of a second phase which looked like ribbons or bunting scattered throughout the structure. The irradiated specimen contained the same large particles. Some grains also contained a much higher concentration of dark spots and loops, similar in appearance and concentration to those in specimens of the same material bulk-heated in a vacuum at 400°C for 2 hr, but larger in size. In the rest of the grains, areas near the large precipitates contained these same spots and loops, but areas more remote from the large precipitates contained instead the same high concentration of small, flakelike particles which were appreciably larger than the loops. These flakes looked like much smaller versions of the large precipitates. Both appeared to be thin disks lying parallel to the {100} planes of the iron. These precipitates (Figure 49) are identical in appearance and habit to the phase Fe_{16}N_2 , observed by Keh and Wriedt [*Trans. AIME* 224, 560 (1962)].

A specimen of the same material was subjected to the same thinning and heating procedure except that it was quenched in a stream of helium

Figure 49. Iron nitride in remelted iron irradiated to 2×10^{20} nvt, heated at 400°C for 2 hr in NH_3 , and furnace-cooled.

instead of being furnace-cooled after being heated in ammonia at 400°C for 2 hr. The specimen contained small spots identical in size and concentration to those in a specimen of the same material bulk-heated in a vacuum. No second phase was observed, which indicated that the nitrogen added had been retained in supersaturated solid solution by the quench.

The results of this set of experiments indicate that nitrogen is not capable of transforming "convertible" radiation defects in iron into loop-forming defects, and that therefore the loop-forming defects do not contain nitrogen atoms. The results also indicate that the radiation-produced nucleation sites for aggregation of loop-forming defects are capable of serving as nuclei for precipitation of iron nitride from a supersaturated solid solution of nitrogen in α -iron. Therefore ambient-temperature irradiation of a supersaturated iron-nitrogen alloy should produce accelerated nitride precipitation similar to the accelerated carbide precipitation observed by Wagenblast and Damask [*Phys. Chem. Solids* 23, 221 (1962)] during ambient-temperature irradiation of a supersaturated iron-carbon alloy. Thus irradiation of iron containing an appreciable concentration of nitrogen (e.g., 0.001 wt %) at temperatures appreciably higher than room temperature (e.g., 60° to 100°C) could yield structures similar to the spots and loops due to oxygen by precipitation of nitrides after the irradiation.

In specimens of irradiated remelted Ferrovac E thinned to 0.002 in. and then heated at 400°C for 2 hr in hydrogen or in methane before being thinned to electron transparency, the spot area was not increased over that observed in bulk specimens heated in a vacuum. These results indicate that neither carbon nor hydrogen can transform "convertible" defects into loop-forming defects and that probably neither is present in the loop-forming defects. The location of the added carbon, which should have precipitated in the methane-treated specimen during furnace-cooling from 400°C , remains a mystery.

In summary, the results of these experiments indicate that the loop-forming defect is a combination of Frenkel defects or defect clusters that survive ambient temperature irradiation and of oxygen atoms, but not carbon, nitrogen, or hydrogen atoms. The increase in yield stress produced by the irradiation does not appear to be greatly affected by whether or not the surviving Frenkel defects are combined with oxygen. In the purified iron containing <35 oxygen atoms per 10^6 iron atoms, the maximum loop area corresponded to ≥ 10 Frenkel defects per 10^6 iron atoms, assuming that each loop surrounded a single-layered disk of point defects, and that the average iron film thickness was $<2000 \text{ \AA}$. Thus the loop-forming defects contain <3.5 oxygen atoms per Frenkel defect.

It has not yet been determined whether the Frenkel defects that combine with oxygen to form the loop-forming defects are vacancies or iron interstitials. Attempts to determine the sense of the loops by tilting-stage techniques have not been successful because of the difficulty in seeing whether the small loops are resolved on the fluorescent screen of the electron microscope. A device that electrically tilts the electron beam in the RCA microscope is being tested; if this device improves the resolution of the instrument in dark-field illumination, determination of the sense of the loops by use of the dark-field technique should be possible.

Correlation of Defect Structures With Mechanical Properties

A series of investigations was started to study the relationship between the radiation defect structures in iron detectable by electron microscopy after postirradiation heat treatment and the changes in mechanical properties resulting from such heat treatment. In initial experiments, Rockwell Superficial 15-T hardnesses are being measured at room temperature on the unstrained shoulders of fractured irradiated tensile test bars heated under vacuum at a constant temperature of 300°, 350°, or 400°C for selected periods of time within the range over which the defect structures have been observed. It is hoped that the results of these experiments will permit distinguishing between the effects of visible and invisible defects on the properties, and, by yielding information on the annealing behavior of the different defects, will help to identify the defects.

Results to date have not been completely analyzed in detail. They have revealed some interesting relationships, however. In Ferrovac E irradiated to 2×10^{18} nvt in which no spots or loops could be detected after postirradiation heat treatment, the irradiation-induced increase in hardness was completely removed after 15 min at 400°C. In Ferrovac E irradiated to 1×10^{19} nvt, in which relatively small concentrations of spots or loops were observed after postirradiation heat treatment, $\approx 80\%$ of the radiation-induced increase in hardness was removed after 8 hr at 400°C, but no further loss in hardness was observed after further heating to 96 hr. In Ferrovac E irradiated to 2×10^{20} nvt, in which the highest concentrations of loop-forming defects were observed after postirradiation heat treatment, $< 60\%$ of the radiation-induced increase in hardness was

removed after heating at 400°C for 96 hr, and loops persisted in the microstructure. In purified iron irradiated to 2×10^{20} nvt, in which a relatively low concentration of loop-forming defects was observed after postirradiation heat treatment, $\approx 50\%$ of the radiation-induced increase in hardness was removed after 15 min at 400°C, and 100% was removed after 16 hr at 400°C, which corresponded to the time at 400°C required to remove the loops. These results indicate that visible aggregates of the loop-forming defects have an appreciable effect in increasing the hardness of iron. In addition, increasing the concentration of loop-forming defects by changing the composition of the iron or by increasing the radiation dose increases the time of annealing required to restore the hardness to the preirradiated value. The results also indicate that the invisible "convertible" defects present in the 2×10^{20} nvt-irradiated purified iron disappear from the iron lattice without forming visible aggregates during postirradiation annealing, and that their rate of disappearance is probably faster and certainly not slower than that of the loop-forming defects. At 350°C, annealing rates for these materials were generally slower. In Ferrovac E irradiated to 2×10^{18} nvt and 1×10^{19} nvt, calculations of the activation energy for annealing based on the ratios of the times required at 350° and 480°C to remove a constant fraction of the radiation-induced increase in hardness yield fairly consistent values of $\approx 30,000$ cal/mole. The data from the 2×10^{20} nvt-irradiated Ferrovac E and purified iron do not yield consistent values. Postirradiation heat treatments at 300°C for periods up to 8 hr have not caused any appreciable reduction in hardness from the as-irradiated values for these materials.

Effects of Radiation on Dislocation Substructures

Dislocation substructures in Ferrovac E resulting from tensile deformation at room temperature to strains between yielding and fracture were examined in unirradiated specimens and in specimens irradiated to 2×10^{18} nvt, 1×10^{19} nvt, and 2×10^{20} nvt. These specimens were obtained by cutting slices from the strained portions of contoured tensile test bars tested to fracture by J.G.Y. Chow and S.B. McRickard. The strain level at the center of each slice could be determined from its precisely known position along the bar from the measurements used to calculate the stress-strain curve for the bar. No gross effects of irradiation on the dislocation structures were detected except

that, as in the previously reported case of specimens strained in compression, the flakelike structure believed to be dislocations surrounding internal sources which appeared on initial deformation of unirradiated specimens was not present in irradiated specimens.

Additional specimens were prepared from similar irradiated and unirradiated test bars of Ferrovac E having different grain sizes. Some of these were examined to see whether variations in grain size or the heat treatments used to obtain these variations could affect the relationships between dislocation structure, strain level, and radiation dose. In the course of these examinations, it was found that the electrolytic thinning technique which had previously produced smooth surfaces on the thinned iron had begun to produce rough surfaces having texture that seriously interfered with the interpretation of internal structure. Much time and effort have been spent to determine the cause of this difficulty and find a cure, without consistent success. When consistently smooth polishes can be obtained, this series of experiments will be con-

tinued and extended to include the effects of temperature of deformation.
J. BRYNER

High-Temperature Reactor Core Materials Studies

Work in this area during 1965 included studies of Br- and Rb-graphite lamellar compounds, the thermodynamic and electrical properties of carbides, nitrides, and phosphides of Th, and the carbides of Zr.

LAMELLAR COMPOUNDS OF GRAPHITE

The rates of isotopic exchange of normal and radioactive Br in the Br-graphite lamellar compounds were measured at temperatures from 20° to 45°C. Natural graphite flakes ranging in size from 50 to 2000 μ were used to prepare the compound C_8Br .

The typical dependence of the rate of exchange on particle size is shown in Figure 50 as a plot of the log rate of exchange at 20°C vs the log of the particle size. The particle size dependence obtained from the slope of this plot is proportional to $1/a$ at large particle sizes and changes abruptly to $1/a^2$ at small particle sizes, where a is the particle diameter.

A plot of the log rate of exchange (normalized to 35°C) for several particle sizes vs the reciprocal temperature is shown in Figure 51. The activation energy obtained from the slope of this plot varied from 7 kcal/g-mole at the highest temperatures to 21 kcal/g-mole at the lowest.

The complex dependence of the rate of exchange on particle size and temperature and the form of the exchange curve has been explained by a surface exchange mechanism. The proposed mechanism assumes that flakes $>300 \mu$ have a mosaic structure of smaller units or crystallites. Particles $<300 \mu$ are single crystallites, i.e., they contain no well-defined grain boundaries. The c -axis thickness of the Br-graphite flakes is assumed to be proportional to the diameter of the flakes, as was found in the case of natural graphite.

This study and the previous study of the kinetics of decomposition of Cs-graphite indicate a high mobility of Cs and Br in the respective graphite compounds, since surface processes rather than bulk diffusion are the rate-limiting steps in each case.

Figure 50. Dependence of the rate of bromine exchange on particle size.

Studies were begun of the kinetics of decomposition and the thermodynamic properties of Rb-graphite compounds. The mechanism of decomposition is the same as that observed in the Cs-graphite system. The compound $C_{10}Rb$ exists in the Rb-graphite as well as the Cs-graphite system. There is preliminary evidence that the stable phases below $C_{10}Rb$ are not the same as those in the Cs-graphite system. Severe attack of the quartz apparatus by Rb caused these experiments to be postponed until an apparatus fabricated from Ni is completed. Detailed descriptions of the experimental techniques and of the completed work are available in the references appended to this section of the report.

THERMODYNAMIC PROPERTIES OF REFRACTORY METAL COMPOUNDS

The thermodynamic properties of refractory metal compounds having potential nuclear application at high temperatures are being studied. The objectives of the investigation are to obtain information on the reactivity and stability of these materials and to increase understanding of their physical and chemical properties.

Figure 51. Dependence of the rate of bromine exchange on temperature.

Thermodynamic data in the thorium-boron system were obtained by using the following emf cells.

- I. $Th, ThF_4 | CaF_2 | ThF_4, ThB_6, B$;
- II. $Th, ThF_4 | CaF_2 | ThF_4, ThB_6, ThB_4$;
- III. $Th, ThF_4 | CaF_2 | ThF_4, ThB_4, Th_\alpha$.

Th_α represents Th metal containing dissolved B in equilibrium with ThB_4 . The emf values obtained with these cells at 800° to 950° C are shown in Figure 52. The standard molar free energies of formation of ThB_4 and ThB_6 at 850° C calculated from the data on cells I and II in Figure 52 are -52.0 kcal/g-atom Th and -54.4 kcal/g-atom Th respectively.

Free energy data are currently being obtained on the thorium-nitrogen, thorium-phosphorus and zirconium-carbon systems with use of emf cells of the following types.

- IV. $Th, ThF_4 | CaF_2 | ThN_x$;
- V. $Th, ThF_4 | CaF_2 | ThP_x$;
- VI. $Zr, ZrF_4 | CaF_2 | ZrC_x$;
- VII. $Th | (CaF_2 + ThF_4) | ThP_x$.

The half-cell on the right-hand side represents either one phase or two phases in equilibrium in the system specified.

Construction of a high-temperature x-ray diffraction unit has been completed. Measurements of lattice parameters and line intensities as a function of temperature will be made on the com-

Figure 52. Emf of cells containing thorium borides.

Figure 53. Vacuum hot-press chamber without cover, showing the graphite susceptor, induction coils, and water-coated shield inside the chamber, and the vacuum valve, water feed-through, induction leads feed-through, valves for admitting inert gas to chamber, and thermocouple feedthrough outside the chamber. The chamber diameter is 12 in.

Figure 54. Vacuum hot-press chamber assembled. The dome contains a site port (left) and a compression-type seal on top which permits a $\frac{3}{4}$ -in.-diam steel rod to move under pressure. The steel rod is connected by a graphite rod to the die plunger. In operation the assembled chamber is situated between the platens of a 30-ton-capacity hydraulic press.

pounds whose thermodynamic properties are under investigation. The combined studies will yield a coordinated body of information on phase equilibria and thermodynamic and thermal properties

S. ARONSON

ELECTRICAL PROPERTIES OF REFRACTORY METAL COMPOUNDS

The program to measure the electrical properties of nonstoichiometric thorium carbide has been a major effort during the past year. Much time was spent in developing techniques for preparing sound, dense, ThC samples suitable for electrical measurement. The techniques evolved consisted of first preparing a sinterable ThC powder of the desired stoichiometry and then hot-pressing the powder in inert dies to form a dense specimen.

ThC powder is prepared by reacting Th metal and graphite powder mixtures at 1700°C to 1800°C *in vacuo*. The carbide powder is hand-crushed to -20 mesh (0.5 mm) and then is crushed in a steel vibratory-type crusher using steel balls. The powder is then ready for pressing.

To eliminate reactions during hot-pressing, the carbides are pressed in dense aluminum oxide dies. Temperatures up to 1400°C and pressures around 5000 psi are used. An all-metal, inductively heated, vacuum hot-press was constructed for fabricating the carbide specimens. The hot-press is shown open in Figure 53 and assembled in Figure 54. With these methods it has been possible to fabricate ThC specimens to as high as 99% theoretical density.

ThC samples about $1 \times \frac{1}{4} \times \frac{1}{16}$ in. have been fabricated over the nominal composition range ThC_{0.74} to ThC_{0.94}. The samples are ground smooth after fabrication, and lattice parameter measurements are made on the ground surface. The lattice parameter is used to characterize the composition in lieu of chemical analysis [S. ARONSON AND J. SADOFSKY, *J. Inorg. Nucl. Chem.* **27**, 1769-78 (1965)]. The resistivity, thermoelectric power, and Hall coefficient were measured by conventional dc methods.

The electrical measurements were made after annealing the samples for 8 hr *in vacuo* at 1800°C . The resistivity increased as the carbon content increased, from $\approx 150 \mu\Omega\text{-cm}$ at ThC_{0.74} to $\approx 185 \mu\Omega\text{-cm}$ at ThC_{0.94} at room temperature. The Hall coefficients behave similarly. They increased negatively from $\approx -6 \times 10^{-4} \text{ cm}^3/\text{coulomb}$ for ThC_{0.74} to $-14 \text{ cm}^3/\text{coulomb}$ at ThC_{0.94} at -196°C .

Figure 55. Electrical resistivity and Hall coefficient of nonstoichiometric thorium carbide. Compositions indicated are approximate.

These results are shown in Figure 55, where the properties at room temperature and at -196°C are plotted against the lattice parameter.

The values observed for the resistivity of ThC are in the range of values reported for titanium carbide (W.S. WILLIAMS AND R.G. LYE, *U.S. Air Force Report ML-TDR-64-25*, Union Carbide Corp., March 1964). However, we observe an important difference: the resistivity of TiC decreases with increasing carbon content, unlike our results on ThC. This TiC behavior suggests that carbon vacancies are the major sources of scattering (*op. cit.*). Our resistivity results do not support this hypothesis. In addition, the Hall coefficient measurements on nonstoichiometric ThC suggests the reason for the increase in resistivity with carbon content. From the Hall coefficient, by using the single band model for conductivity, the number of conduction electrons can be calculated. As the Hall coefficient increases with increasing carbon content, as seen in Figure 55, the number of conduction electrons decreases proportionately. Thus our observed increase in resistivity with added carbon is consistent with a decrease in the number of conduction electrons.

The number of conduction electrons calculated from the Hall coefficients is ≈ 0.2 electrons/Th atom. This value is similar to results on TiC, ZrC, and HfC [T. TSUCHIDA ET AL., *J. Phys. Soc. Japan* 16, 2453 (1961)] and indicates that the electronic structure of ThC is similar to that of the Group IV transition metal carbides.

The decrease in the number of conduction electrons as carbon is added to nonstoichiometric ThC is not explained by current band structure descriptions of the monocarbides (J. PIPER, in *Intern. Symp. Compounds of Interest in Nuclear Technology*, pp. 29-43, AIME, 1964). These descriptions appear satisfactory for transition metal carbides and nitrides with valence electron concentrations >8 . (The valence electron concentration is the sum of the nominal valences of the metal and nonmetal, i.e., 4 electrons for Th and 4 for carbon.) For these materials, additional valence electrons start to fill a new band and they contribute directly to conductivity. For nonstoichiometric ThC with the valence electron concentration <8 , adding carbon apparently affects the band structure in such a way that fewer conduction electrons result.

The region of valence electron concentration >8 is now being investigated by partially substituting nitrogen (with 5 valence electrons) for carbon to form thorium carbonitrides.

A. AUSKERN, S. ARONSON, J. SADOFSKY, F. SALZANO

Reactor Monitoring

Reactor Monitoring programs on the graphite reactor were continued, and a program for monitoring the core materials in the HFBR was begun in 1965.

DIMENSIONAL CHANGES (BGRR)

Monitoring Samples

The graphite monitoring samples have continued to recover significant portions of the radiation-induced dimensional expansions. Length-change measurements were obtained for specimens dispersed throughout the BGRR over a wide range of operating temperatures and neutron flux. More than 200 cylindrical samples ($\frac{3}{4}$ in. in diam by 4 in. long) were measured with use of an optical comparator after every other reactor operating and annealing cycle. The effectiveness of the annealing procedures was thus determined. Results for typical graphite samples are shown in Table 10. They indicate the continued effectiveness of the frequent (monthly) annealing program. All samples have contracted. In addition, most samples have had more radiation damage removed than had been introduced by the neutron irradiation during the previous period. Column 5 shows

Table 10

Dimensional Recovery of BGRR Monitoring Samples After 42 Monthly Anneals

Channel	Approx. irrad. temp., °C	Distance from pile gap, in.	Total exposure ^a to 6/15/62, MWD/Ct ^c	Total growth ^b to 6/15/62, in. $\times 10^4$	Additional exposure since 6/15/62, MWD/Ct ^c	Net recovery of total growth, ^b %
B-3½ N	28	4	1440	108	661	67.2
B-3½ N	85	30	1480	77	660	70.6
B-3½ S	80	30	1480	82	669	59.7
B-3½ S	125	56	1380	54	626	61.7
B-0-4½ N	76	22	2020	169	647	42.9
B-0-4½ S	95	32	1990	109	630	46.6
B-1-4½ N	95	28	400	61	698	36.8
B-1-4½ S	120	45	1060	46	743	51.2
B-4½ N	100	43	763	57	208	46.2
B-4½ S	125	55	660	54	199	58.8

^aBeginning of Frequent Annealing Program.^bAs of May 19, 1965.^c1 MWD/Ct is equivalent to 7×10^{16} nvt ($E > 0.6$ MeV).

the sample growth at the beginning of the frequent annealing program (June 15, 1962). The sample contractions due to this annealing program are shown in column 7 as % net recovery. These values already include expansions due to the irradiation alone during this period (column 6). Many samples are now approaching their preirradiation dimensions.

BGRR Height Measurements

The reactor height changes are determined at three different BGRR locations. These locations and their associated maximum increases in height (which occurred late in 1962) are shown in Table 11. The present increases in reactor height above the original height of 25 ft are indicated in column 3. The last column (% recovery) shows the effectiveness of the annealing program in controlling the height of the moderator structure. The results reported here are for the highest point (5 in. north of the central gap) in each of the 3 horizontal channels.

BGRR Central Coolant Gap

The central gap through which all coolant air reaches the moderator and fuel during normal operation has consistently widened during the past year. The gap width at the start of the frequent annealing program (June 15, 1962) was 2.159 in., compared with an original value of 3.150 in. The

present gap width of 2.330 in. reflects a recovery of 17% during the frequent annealing program.

STORED ENERGY (BGRR)

Releases up to 350°C

Stored energy releases up to 350°C are of interest because portions of the moderator structure reach this temperature during annealing runs. These stored energy results are obtained by linear-rise calorimetry techniques. Samples that have followed reactor history and were irradiated in the BGRR at 30° to 75°C were examined for stored energy releases at 200°C and at 350°C. No significant releases were observed at these temperatures.

Total Stored Energy

Total stored energy (above 400°C) values were obtained for graphite specimens mined from the moderator in the regions of highest flux and lowest operating temperatures. The heat of combustion values from which the stored energy is determined were compared with those for samples from this area previously examined by the same technique. No significant changes in the total stored energy for this region were observed. In addition, the distribution of this stored energy in relatively narrow temperature regions up to the temperature at which all stored energy is finally released was

Table 11

Height Changes for the Brookhaven Graphite Research Reactor

Location	Maximum increase in height, in.	Present increase in height, in.	% Recovery
A-6-15	1.075	0.844	21
B-0-15	1.021	0.772	24
B-6-15	0.956	0.735	23

examined. The releases were determined every 200°C up to 1600°C; stored energy released in each region did not exceed the specific heat of graphite.

BGRR LOW-TEMPERATURE IRRADIATION FACILITY

Construction and testing of the vertical irradiation facility continue. This facility will permit irradiation of many materials at temperatures close to that of liquid nitrogen.

The facility is being constructed with the following design features.

1. A vacuum-insulated cryostat with a primary cooling system filled with pure, dry nitrogen gas at a pressure of ≈ 1.5 atm (in-pile portion).
2. A heat exchanger with a secondary cooling system which will use commercial liquid nitrogen at no overpressure (out-of-pile portion).
3. Automatic filling of the secondary system.

HFBR MATERIALS SURVEILLANCE PROGRAM

Aluminum Reactor Vessel Material

The HFBR pressure vessel is constructed of type 6061-T6 aluminum. It contains the active core, reflector, coolant, and control elements and provides space for the experimental facilities that utilize the high neutron flux.

The maximum neutron irradiation exposure of the vessel will occur at the tip of horizontal beam tube H-1 at a calculated temperature of 150°C.

A program has been initiated to measure the effects of irradiation on the mechanical properties of samples made from this material. It will consist of irradiating 5 units in the HFBR, each containing 12 samples operating at 3 different temperatures (4 samples at each temperature). The program will provide information on the condi-

tions existing at the tip of beam tube H-1 during full power operation and after long exposures. Temperatures between 120° and 205°C will be obtained through regulation and control of mixtures of helium-nitrogen gases flowing in a fixed annulus around the samples.

Steel Thermal Shield Materials

The HFBR thermal shield consists principally of SA201 (carbon silicon) steel plates. It provides protection against excessive heating of the concrete shielding, supports the reactor vessel, and provides containment for D₂O leakage or for any other reactor vessel accident. The shield is composed of a multiple-wall vessel containing H₂O passages between some shells and a layer of lead between others. The operating temperature of the steel plate structure is expected to range from 55° to 85°C.

A program has been initiated to determine the upward shift in the nil ductility transition temperature for specimens irradiated to an equivalent 25-yr HFBR exposure (5×10^{18} fast nvt). Samples have been chosen around the circumference of the inner and thickest wall plates of the thermal shield, at the horizontal midplane of the reactor. The experiment will be conducted in BGRR facility B-2-4½ at an approximate instantaneous fast flux of 4×10^{11} nvt. Total exposure after irradiation for 6 to 8 months will be 5×10^{18} nvt (fast). Irradiation temperature will be $< 85^\circ\text{C}$. The actual flux and temperature conditions for this facility will be determined from prior irradiation of an instrumented mock-up package. Flux monitors (iron and depleted uranium), however, will be included in the final capsules.

HFBR DUAL IRRADIATION FACILITY

A program to provide new experimental facilities for the HFBR has been initiated. The instrumentation and equipment will provide means for studying radiation-induced property changes of many materials under known, controlled conditions. The proposed double-chambered irradiation thimble and its accessory equipment will include the following features:

1. A means for introduction, regulation, and control of up to six different mixtures of helium and nitrogen gases in the dual facility; this feature will permit a wide range of controlled environments and irradiation temperatures for each experiment.

2. Instrumentation for recording and controlling temperatures through the introduction of up to 12 thermocouples into the new facility.

3. A means for independent charging, operation, and discharging of experiments in each side of the dual facility; if desired, this feature could permit irradiation of nonrelated experiments in each half of the new facility.

4. A means of monitoring for experimental changes. Temperature, pressure, and flow conditions for any experiment can be continuously examined for compliance with HFBR safety requirements.

R. SINGER

Metallography

Metallographic work during 1965 consisted primarily of routine examination of samples described elsewhere in this report. Several examples of more than routine interest are described below. Irradiation effects studies using the field ion microscope were begun.

FAILURE IN COSMOTRON MOTOR GENERATOR

A failure occurred in the copper windings at the rear of the Cosmotron motor generator. The dismantled portions of the affected region were examined metallographically to determine the cause of failure.

Several bars were sectioned perpendicular to the failure. Three bars completely separated during cutting. The fourth bar (Figure 56) remained intact; a crack can be seen that has propagated $\approx 90\%$ across the section. Microscopic examination revealed no unusual conditions in the region of failure. Microhardness measurements indicated a slight increase in hardness adjacent to the crack.

This failure can be attributed to fatigue; the notch where the crack initiated probably acted as a stress raiser to initiate the crack. The 30×10^6 cycles during the life of the generator probably produced the fatigue failure.

METEORITE STUDIES

In conjunction with the Chemistry group conducting meteorite studies, techniques were developed whereby dissimilar materials could be polished with little or no relief. This condition must be maintained if the specimens are to be successfully analyzed in the electron-probe microana-

lyzer. A silk polishing lap, applied to a vibratory polisher and impregnated with diamond abrasive, produced the best surface for these purposes.

J. SADOFSKY, O. KAMMERER

THERMODYNAMIC PROPERTIES OF NONSTOICHIOMETRIC THORIUM MONOCARBIDE

As part of the work in the ThC system, >100 specimens were examined to determine accurate lattice parameters.

Each sample was placed in a specially constructed radiation shield encased in a thin Mylar film to protect it from air and water vapor. During each run the chamber was continually flushed with helium gas.

Lattice parameters were calculated by using a modified Nelson-Reilly extrapolation. The value of α_0 extrapolated $-\omega\theta = 90^\circ$ was precise to $\pm 0.001 \text{ \AA}$.

S. ARONSON, J. SADOFSKY

FIELD ION MICROSCOPE

Studies of neutron irradiation effects on tungsten using the field ion microscope have been in-

Figure 56. Fatigue crack in bar removed from copper windings at rear of Cosmotron motor generator. ($0.9\times$.)

Figure 57. Field ion pattern obtained from G.E. 218 W tip, irradiated to 10^{17} nvt fast neutrons ($E > 1$ MeV). Circled area indicates zone of damage. ($0.85 \times 10^6 \times$)

initiated. Field ion micrographs of W irradiated to 10^{17} nvt fast neutrons ($E > 1$ MeV) exhibit dark zones from 50 to 60 Å in diameter. Surrounding these zones are bright emitting regions interpreted as small interstitial clusters. A pattern for a typical specimen is shown in Figure 57; the area of interest is indicated. These small clusters are observed as di-interstitials. The size of the damage zones seems to decrease upon annealing through stage III recovery. Preliminary results on W exposed to

10^{16} nvt fast neutrons indicate a decrease in damage zone size with decreased exposure. Observations on higher exposures will be forthcoming. Attempts are also in progress to see if the zone size is dependent on irradiation temperature.

Electron microscope observations of the irradiated material are also being undertaken, and an attempt will be made to correlate them with the results of the field ion microscope.

Under way at present is the construction of a liquid-helium stainless steel microscope which will permit observation of other nonrefractory metals.

M. ATTARDO, J. SADOFSKY

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Engineering Division

T.V. SHEEHAN

The Engineering Division of the Department is a service organization supporting departmental research programs. About 50 persons are involved in engineering, design, construction, and operation of experimental equipment. The Division also contributes to ANS Standards Committees, ASME Committees, AEC Sodium Components Development Committee, and the *High-Temperature Liquid-Metal Technology Review*.

Work was done for the Reactor Physics Division on the Mark II Source Reactor, heavy water exponential system, and control rod mechanism for the SCHIZO reactor.

On the HFBR project, members of the Division have continued to assist the Reactor Division in the preoperational program. In addition, the control system for the four air locks was redesigned including power actuators, automatic latches, and an emergency pneumatic power supply.

A preliminary flowsheet has been prepared for the HFBR intermediate loop. This system will circulate demineralized water to remove heat from the primary system and dump it into the cooling tower water circuit. A specification has been prepared for the secondary heat exchangers and estimating proposals have been solicited.

A facility to permit the irradiation of tensile test specimens at controlled temperature is being designed for the HFBR materials surveillance program. The facility will be installed in the HFBR V-13 core edge irradiation thimble.

The design and construction of a monitor foil irradiation facility, for use in the HFBR V-10 thermal irradiation thimble, has been completed. The facility will be used to irradiate flux monitor foils in conjunction with the HFBR beam tube flux calibration experiments. Approximately 50 irradiations will be conducted during the low power runs.

A 100-gal stainless steel gas-liquid separator was designed for installation in the off-gas line from the HFBR reactor vessel. The separator will be located between the reactor vessel and the safety relief valves to trap heavy water carried out of the reactor vessel during depressurizations.

A major Radiation Division project worked on was the chemonuclear loop. This facility will be installed in the BGRR to study gas-phase chemical reactions using fission fragments as an energy source. The component test loop was completed and operated allowing final component selections to be made. Major assemblies and components have been designed and are being fabricated. Equipment to remove the radioactive in-pile section from the reactor has been built and tested, and the vent tank system was installed in the reactor yard. Work is continuing on instrumentation, shielding, process piping, and various rigging and auxiliary apparatus.

Development work on the standardized cobalt sources for the Radiation Division was completed. These Mark II sources have the primary encapsulation metallurgically bonded to the cobalt to allow specific activities up to 400 Ci/g.

A Co⁶⁰ blood irradiator has been designed. This semipermanent facility, weighing 5 tons, will be located in the Medical Department.

Other work for the Radiation Division included the design of a gamma monochromator, design of source plaques for the HIRDL irradiation cell, and the evaluation of a portable irradiator built for the Division of Isotope Development.

In the settled bed reactor program, in-pile capsule irradiation support continued. The sixth capsule is being irradiated in the BGRR. This capsule was modified to use a gas-filled annulus for temperature control. In addition, three capsules have been irradiated at the Engineering Test Reactor (ETR) at Idaho Falls, Idaho. More equipment is now being installed at the ETR to expand this work. The water test loop for the settled bed reactor program was enlarged to accommodate an ordered bed fuel assembly. The new assembly has been installed and is ready for testing. Engineering assistance has continued on the 1000-MW(e) ordered bed reactor.

Zircaloy-clad Pu-Al fuel elements were procured for the Reactor Physics Division.

Engineering support for the Chemistry Department's solar neutrino experiment was continued.

This project involves the erection of a 100,000-gal capacity vessel with liquid and gas circulating systems in a deep mine in South Dakota. The site has been prepared, erection of the vessel is in progress, and the control system has been designed.

During the year, the following work was done on the heat transfer facilities of the Chemistry and Chemical Engineering Division. The boiling potassium heat transfer loop was modified and returned to service. New operating parameters for this facility are being investigated. The NaK heat transfer loop was modified to include a cross flow rod bundle test section. This test section was installed including an additional instrument panel. The loop is now operating. An additional cross flow rod bundle test section with the rods at a 45° angle away from the direction of flow is currently under construction. An eccentric annulus test section was completed and installed in the mercury loop. The rod bundle test section is being modified to provide eccentric locations for test elements. In addition to routine engineering support, the following assistance was given to the Metallurgy Division. The pumped boiling liquid-metal loop has been converted from a sodium system to cesium. A new turbine simulator vapor impinge-

ment test section was designed and installed. Final installation of the loop into the vacuum chamber is under way. The instrument panel from the natural circulation boiling sodium loop is being revised for service with this loop. Preliminary work has begun on two liquid sodium corrosion loops. These loops are to be constructed of 316 SS and will be used for fast reactor materials studies.

In addition to the project assistance mentioned above, instrumentation and control systems have been designed, specifications prepared, and panels fabricated for extractive distillation, radiation polymerization, vacuum chamber control, and flashing orifice experiments.

The following are two engineering studies completed for the Department. A study of various MPD (magneto plasma dynamic) generating systems has been completed. A scoping design and cycle analysis was done for two concepts; one involving fission induced ionization and another utilizing nitrogen recombination energy to increase the gas conductivity. A conceptual design of a rotating fluidized bed research reactor has been prepared. After operating for periods of ≈ 1 min at 5000 MW, a peak thermal neutron flux of 4×10^{16} neutrons/cm²-sec can be attained.