TID-2502 (Del.)

MASTER

NUCLEAR SCIENCE AND TECHNOLOGY

Extracts from Reactor Science and Technology,
Volume 1, Issues 1 to 3 (April - December 1951)

LEGAL NOTICE

This report was prepared as an account of Government sponsored work. Neither the United States, nor the Commission, nor any person acting on behalf of the Commission:

A. Makes any warranty or representation, expressed or implied, with respect to the accuracy, completeness, or usefulness of the information contained in this report, or that the use of any information, apparatus, method, or process disclosed in this report may not infringe privately owned rights; or

B. Assumes any liabilities with respect to the use of, or for damages resulting from the use of any information, apparatus, method, or process disclosed in this report.

As used in the above, "person acting on behalf of the Commission" includes any employee or contractor of the Commission, or employee of such contractor, to the extent that such employee or contractor of the Commission, or employee of such contractor prepares, disseminates, or provides access to, any information pursuant to his employment or contract with the Commission, or his employment with such contractor.

ATOMIC ENERGY COMMISSION
UNITED STATES OF AMERICA

Photostat Price $ 41.40
Microfilm Price $ 11.10

Available from the
Office of Technical Services
Department of Commerce
Washington 25, D. C.

MASTER

LEGAL NOTICE

This report was prepared as an account of Government sponsored work. Neither the United States, nor the Commission, nor any person acting on behalf of the Commission:

A. Makes any warranty or representation, express or implied, with respect to the accuracy, completeness, or usefulness of the information contained in this report, or that the use of any information, apparatus, method, or process disclosed in this report may not infringe privately owned rights; or

B. Assumes any liabilities with respect to the use of, or for damages resulting from the use of any information, apparatus, method, or process disclosed in this report.

As used in the above, "person acting on behalf of the Commission" includes any employee or contractor of the Commission to the extent that such employee or contractor prepares, handles or distributes, or provides access to, any information pursuant to his employment or contract with the Commission.

MASTER

MASTER

DECLASSIFIED

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

~~CONFIDENTIAL~~

Subject Category, REACTORS-RESEARCH AND POWER.

This report has been reviewed under the Declassification Guide of 1955.

Do Not Photostat

The Atomic Energy Commiss[illegible] representation or warranty as to the accuracy or usefulness [illegible] tion or statements contained in this report, or that the use [illegible] nation, apparatus, method or process disclosed in this repo[illegible] fringe privately-owned rights. The Commission assumes n[illegible] th respect to the use of, or for damages resulting from th[illegible] information, apparatus, method or process disclosed in this [illegible]

This repo[illegible] been reproduced directly from the best available copy.

Printed in USA, Charge $1.10. Available from Technical Information Service, Industrial Request Section, P. O. Box 1001, Oak Ridge, Tenn. Please direct to the same address inquiries covering the procurement of classified AEC reports.

~~CONFIDENTI t~~

CONTENTS

ARTICLES

DECLASSIFIED

CONTENTS

ARTICLES

REACTOR FUTURES

TECHNICAL NOTES

714 003

CONFIDENTIAL

CONTENTS

TECHNICAL NOTES

CONFIDENTIAL

DECLASSIFIED

INTRODUCTION

The new classification guide of the Atomic Energy Commission places the majority of information on reactor technology and related subjects in the "Confidential" category. Much of the material in back issues of the Journal of Nuclear Science and Technology and its predecessors, the Journal of Metallurgy and Ceramics and the Journal of Reactor Science and Technology, falls into this category. In order to make such information readily available to those possessing a suitable clearance, articles from these earlier issues are being reissued as Gray Area Journals as follows:

TID-2501	JMC, Issues 1 thru 6 (TID-65 thru 69), July 1948 - January 1951
TID-2502	RST, Vol. 1, Issues 1 thru 3 (TID-71 thru 73), April 1951 - December 1951
TID-2503	RST, Vol. 2, Issues 1 thru 4 (TID-2001 thru 2004), April 1952 - December 1952
TID-2504	RST, Vol. 3, Issues 1 thru 4 (TID-2008 thru 2011), March 1953 - December 1953
TID-2505	RST, Vol. 4, Issues 1 thru 4 (TID-2012 thru 2015), March 1954 - December 1954
TID-2505A	Cumulative Index to all "back issue" JMC and RST Gray Area material
TID-2506 Vol. 1A, Issue 1	NST, Vol. 1, Issues 1 thru 3 (TID-2016 thru 2018), February 1955 - June 1955

Due to the many changes which have taken place on the editorial staff of the Journal during its history, it has been considered inadvisable to specify individual credits for material from early issues. In this regard, the present editors would like to acknowledge the fine work of former editors, Bruce S. Old, George L. Weil and Frank R. Ward, through whose efforts most of the material was originally obtained.

DECLASSIFIED

The Reactor Program

By George L. Weil

Special Assistant to the Director, Division of Reactor Development
U. S. Atomic Energy Commission

with Foreword by L. R. Hafstad

Director, Division of Reactor Development
U. S. Atomic Energy Commission

FOREWORD

It is a truism that no one ever seems to learn anything from history. Yet history has many lessons to teach, and the tuition is free. In our field—the field of atomic energy in general and reactor development in particular—a striking fact is that, in spite of much talk about how new, different, and revolutionary this field is, the actual events are retracing in almost tedious detail the pattern set by other major technical developments such as steamships, railroads, airplanes, and submarines.

In early stages when the facts are few, there is the period of violent clash of opinion. Real and self-appointed experts are indistinguishable. A running battle rages between optimists and pessimists, with emotional oscillations from religious fervor to deepest ridicule. Then, with an increasing investment of technical man-years, facts accumulate. They act as a damping coefficient on the oscillations which in due course are reduced to a ripple, and the new development gradually takes its proper place in our society alongside—but not in place of—developments of the past.

In the reactor program we seem to have lived through several cycles of the initial oscillations. We are definitely in the stage of accumulating facts. We are better supplied now with scientific facts than with engineering facts. The latter can be acquired only by building and operating reactors of promising types. At this stage it is clear that we have an immediate and continuing need for production reactors of increasingly improved performance. To be able to make the improvements we need a vigorously developing reactor technology. As long as we are building reactors for any purpose, we are developing a reactor technology. Hence we need not be too concerned about the specific uses for which reactors are proposed. Furthermore, history teaches that new uses for reactors will be found—indeed, will find themselves—once the technology is well developed.

Therefore, let us strive for both perspective and tolerance in this controversial activity in which we are engaged. Let us focus our best efforts on completing the long-overdue first generation of reactors now under construction. Then let us make certain that our best collective thinking, based on lessons learned from operating reactors, is incorporated in succeeding generations of reactors so that they will make maximum contribution to our technology and to national strength in the period of desperate trial which lies ahead.

Part I*

INTRODUCTION

Reactor Science and Technology Journal

The primary purpose of the new journal, Reactor Science and Technology, is to provide a medium for dissemination of ideas and of information on activities, technical problems, and progress in reactor development. It is hoped that the journal will advance the reactor art by stimulating new ideas and activities, particularly among those not closely associated with design problems or with specific reactor projects.

Unfortunately, the interchange of ideas among reactor design groups is difficult under the circumstances in which the Commission's program must proceed. The lack of contact of many chemists, metallurgists, physicists, engineers, and other specialists with the reactor program is particularly serious for they could contribute substantially to the work of the reactor designers. It is being recognized more and more that the development of reactors requires close coordination with and contributions from practically all technological fields. This journal will be devoted primarily to promoting such coordination and to encouraging opportunities for contributions to the reactor program from all groups.

The purpose of this article is to present briefly an over-all picture of the Commission's reactor program. With this picture as a background it is planned that other articles in the current and future issues will take up broad phases of the program such as materials production (including breeding), power production (mobile and stationary), and specific projects (homogeneous reactors, reactors for submarine and aircraft propulsion, etc.). In the detailed papers emphasis will be on the technical and design problems that must be solved if reactors are to be developed to meet efficiently the specifications established for each application.

General Features of the Reactor Program

It should be recognized that the current reactor program is composed of two distinct elements having different antecedents. On one hand, we have a program, now rapidly maturing, which was to a large extent determined when the atomic energy business was under the Manhattan Engineer District. In the interest of continuity the MED program was more or less accepted by the Atomic Energy Commission when it assumed responsibility in January 1947. Although some redirections of effort have been instituted by the Commission, the broad features can be readily recognized today. On the other hand, we have a program, still in the early stages, which has been determined entirely under the auspices of the Atomic Energy Commission. For the past several years it has been the Commission's policy to bring the so-called "first generation of reactors" to a successful completion as rapidly as possible. This has demanded a major effort on the part of the staffs of the Commission and its contractors. Today the first generation of reactors is well along in development — in three cases, in various stages of construction.

With regard to the projects which have been redirected, a general guiding trend can be identified, namely, the objectives have been sharpened and established on the basis of short-range needs. For example, the High Flux Reactor has been converted into the Materials Testing Reactor (MTR).

Of the major reactor projects existing in January 1947 the Experimental Breeder Reactor (EBR) is the only one that has survived as originally conceived. The reason for this trend should be clear in the light of the large development and construction costs of major reactor projects and the commitment of the efforts of large, highly trained groups of engineers and scientists over long periods of time. To achieve the long-term stability desirable in a major reactor project requires that the project objective be clearly recognized and accepted by the Commission and the participating contractor groups as one that has an importance commensurate with the anticipated expenditure and commitment of personnel. If this criterion is satisfied, then it is hoped that under "normal" national and international conditions a major project will be redirected only if such a step is called for by the development of new technical information.

With the acceptance of the guiding philosophy discussed above and with the growth of perspective among the Commission's staff, the second and third generations of reactors are now emerging under a considerably better coordinated and planned program than was the case for the first generation. With the first-generation reactors nearing completion, more time is available to the Commission and contractor

---

*Editors' Note: The second and concluding part of this article will appear in the second issue of this journal. Part II will discuss the AEC Reactor Development Program as it relates to mobile and stationary reactors for the production of power and to reactors for research and miscellaneous purposes.

The Reactor Data Chart at the end of this issue tabulates essential data on, and the status of, reactors and reactor designs in the U.S.A. and abroad.

staffs for consideration of long-range objectives and the design and selection of future reactors to meet these objectives.

The current reactor program is presented and discussed in the following section in a framework based on objectives.

General Discussion of Program Planning

The over-all long-range objective of the Commission's reactor-development program may be stated as follows: to investigate, evaluate, and develop all potentially useful applications of atomic energy through operation of reactors. These potentially useful applications can be discussed in three broad categories, namely, (1) production of materials, (2) production of power, and (3) miscellaneous (including research).

Category 1 includes reactors developed primarily for the production of materials. Such reactors produce neutrons available for capture in U^{238} to produce plutonium, in Th^{232} to produce U^{233}, in Li^{6} to produce tritium, and so forth. Useful power may or may not be a by-product. The basic types of reactors considered for such application include converters* and breeders, homogeneous and heterogeneous reactors, thermal-, intermediate-, and fast-neutron-energy reactors, and reactors designed to use all types of fuel.

Category 2 includes reactors developed primarily for the production of useful power for military and industrial purposes. This category also covers reactors designed to supply relatively low-temperature heat for central heating plants or similar applications. Production of fissionable or other materials may or may not be provided as a by-product. Again, as in category 1, all basic types of reactor designs are considered.

Category 3 includes general research reactors, materials-testing reactors, and other reactors designed for special purposes. The types of reactors developed in this category will not, in general, have the potential large-scale uses of those in categories 1 and 2.

Before discussing the individual projects it would be helpful to outline briefly the steps in the development of a reactor and to provide a framework in which the relation of each project to the over-all program and long-range objectives can be viewed. The development of a full-scale reactor from its original conception through its construction can be broken down into a number of phases. A useful breakdown is as follows:

Phase I: Through conceptual design (little, if any, specific component or mock-up work). General feasibility indicated and qualitative performance and cost estimates made.

Phase II: Through preliminary design of prototype or full-scale operating unit (based on program of component studies, heat-transfer measurements, mock-ups, critical assemblies, small-reactor experiments, etc.). Sufficient to provide reasonably firm evaluations of engineering feasibility, performance characteristics, and construction costs.

Phase III: Through detailed design (architect-engineering construction drawings) of prototype or full-scale operating unit, based on extensive experimental program. Firm estimates of cost and performance made.

Phase IV: Through construction of prototype or full-scale operating unit.

In proceeding from phase I through phase IV the number of projects in each phase will obviously diminish rapidly and the required expenditures per project increase rapidly. In phases I and II the many possible concepts for reactors to meet a specific need will be evaluated and weeded out on the basis of engineering feasibility, anticipated performance, cost, and other criteria. Other projects will be terminated in one of the early phases, to be revived if a need develops which would justify assigning the technical effort and the relatively large expenditure of funds required to carry through to more advanced stages.

The phase to which a particular project is to advance will be determined by the relation of the project to other projects and by the importance of its objective. The following is presented as a guide to indicate the major criteria used for establishing the extent of development planned for a project:

Development through Phase I

1. No immediate need for full-scale operating units and little probability that a need will develop in the near future.
2. One of several alternate designs to be evaluated for further development.

Development through Phase II

1. No immediate need for full-scale operating units but a reasonable probability that a need will develop in the near future.
2. Back-up design for projects in more advanced stages of development.
3. One of several alternate designs to be evaluated for further development.

Development through Phase III

No immediate need for full-scale operating units but a strong probability that a need will develop in the near future.

---

*In this article a converter is defined as a reactor that burns one fissionable isotope and produces another, for example, U^{235} burned to produce Pu^{239}. A breeder is defined as a reactor which burns and produces the same fissionable isotope, for example, U^{233} burned to produce U^{233}.

DECLASSIFIED

Development through Phase IV

1. An immediate need for full-scale operating units.
2. A strong probability that a need for full-scale operating units will develop. Information required for proper evaluation of performance can be obtained only by operating a full-scale unit.

THE REACTOR DEVELOPMENT PROGRAM

Production Reactors

The most extensive use of reactors to date has been in the production of plutonium for weapons. In the light of the present world situation it would appear that this use will continue to be important for some time to come. However, the possible large-scale military requirement for other materials, such as tritium, emphasizes the fact that, basically, production reactors are designed to produce large quantities of neutrons. The particular design of a reactor determines how these neutrons will be utilized. Although flexibility of performance has become a desirable characteristic, it can be obtained only at the expense of maximum efficiency of operation.

1. Converters. (a) Plutonium Production (Natural-uranium Fuel). Reactors designed primarily for the purpose of converting U^{235} into other fissionable isotopes (plutonium and U^{233}) are referred to as converters. In cases in which production of plutonium is desired, it turns out that the ratio of U^{235} to U^{238} which occurs in natural uranium is in the range that makes natural uranium a convenient and efficient combination of fuel material (U^{235}) and producer material (U^{238}). However, the use of natural uranium as a fuel element in plutonium-production converters is not necessarily the optimum choice from the point of view of over-all economy and efficiency of operation. With the availability of large quantities of uranium having various degrees of enrichment in the range from less than the natural 0.7 per cent to over 90 per cent, it is no longer necessary to attach to natural uranium a uniqueness other than that determined by its cost. Furthermore, since the fraction of the contained U^{238} that may be consumed per pase of the fuel through the reactor is now limited to only a few per cent by requirements imposed by the weapons' use of the plutonium, consideration must be given to developing the effective utilization of raw materials through combined operation of gaseous diffusion plants and reactors. Thus the uniqueness of natural uranium as a feed for plutonium-producing converters, from the point of view of isotopic mixture, vanishes. However, for a number of reasons all converter reactors for production purposes, both existing and planned, are designed to use natural uranium as fuel.

In contrast to the stringent requirements with regard to neutron economy which are demanded in the design of breeder reactors, the requirements to achieve acceptable performance in the case of U^{235} converters are much less severe. This follows from the fact that the conversion of U^{235} to some other fissionable isotope such as plutonium or U^{233} is an irreversible process. A few per cent improvement in the conversion ratio, i.e., ratio of number of atoms of new fissionable isotope produced to the number of atoms of U^{235} destroyed, can influence the long-range availability of fissionable material only by the same percentage. On the other hand, a few per cent improvement in the breeding ratio will have very significant effects on the long-range fissionable-material picture and may make the difference between having a fairly constant, or even slowly diminishing, world supply of fissionable material or a rapidly increasing supply. In the long term, of course, the availability of uranium and thorium raw materials will limit the over-all supply of fissionable material.

It is, of course, highly desirable from the point of view of efficiency of operation to design converters that have neutron economies as favorable as possible. However, with converters one reaches a point of diminishing returns from effort at a much earlier stage than is the case in the design of breeders. It is also highly desirable to extract useful energy from converter reactors.

Hanford Reactors. At the present time all our plutonium-production facilities, those in operation and those planned, are of the thermal-neutron-energy converter type. The Hanford plants are charged with natural uranium in a graphite moderator and cooled with ordinary water. The choice of the Hanford design was originally dictated by the urgent requirement to achieve large-scale production in the shortest possible time. Although some major improvements in performance have been made and can be anticipated through design changes, these refer principally to increasing the power level per reactor and minimizing operating problems. The fundamental limitation in the Hanford type reactor is the relatively low value of the reproduction factor, k, which can be achieved with the materials of construction and natural uranium as fuel. This limitation determines the degree of flexibility available in design and the maximum utilization of the U^{235} consumed in terms of plutonium produced and excess neutrons available for production of other materials. It is worth pointing out, however, that the Hanford reactors can be successfully operated with enriched uranium by the substitution of aluminum-U^{235} alloy fuel slugs for the natural-uranium slugs. This substitution greatly increases the excess reproduction

DECLASSIFIED

factor of the lattice through the removal of the absorbing, nonfissionable uranium isotope U^{238}. Although large quantities of excess neutrons are thus made available for production of materials such as tritium, this is accomplished by sacrificing plutonium production. The General Electric Company at Hanford is continuously engaged in a program to improve the performance of existing reactors and to make available, if and when needed, the most advanced design.

Savannah River Reactors. The new production reactors, which are being designed by the E. I. du Pont de Nemours & Company and which will be constructed and operated by that company at the Savannah River plant near Augusta, Georgia, will also be of the converter variety. However, since at this time the requirement is not only to produce plutonium but also to provide large quantities of excess neutrons for the possible production of tritium, the new reactors are being designed to provide a much greater degree of flexibility through better neutron economy than the Hanford reactors have. Although the new reactors will be designed to operate with natural uranium as fuel, the greater flexibility is obtained through the use of heavy water as both moderator and coolant and by varying the amount of natural uranium in the reactor. Fuel rods of different sizes can be used, depending on the desired relative production capacities for plutonium and tritium.

The basic design selected for the new converter production reactors was developed at the Argonne National Laboratory. Development work in cooperation with the Du Pont company is continuing at this laboratory. Another basic design using natural-uranium fuel is being developed by the Atomic Energy Research Department of North American Aviation, Inc. This design uses heavy water as a moderator and ordinary water as a coolant. The project is being carried through phase II to provide an alternate back-up design in the event that difficulties arise in proceeding with the heavy water – cooled Argonne-Du Pont design. Although the use of light water complicates the structural design and, because of the less favorable neutron economy compared to use of heavy water, provides less flexibility in engineering design, it may offer a more effective utilization of the heavy water investment.

Homogeneous Plutonium-Production Reactor. A third and different type of basic design using a natural-uranium salt or slurry in heavy water is being investigated at the Oak Ridge National Laboratory. This is a longer range project than the two mentioned above in that the design being studied is homogeneous, as opposed to heterogeneous. The homogeneous type reactors, i.e., those in which the moderator and fuel are intimately mixed instead of being segregated, offer a number of potentially attractive features as plutonium producers. The most noteworthy feature is the potentially highly favorable neutron economy. The term "potential" will be used frequently when referring to homogeneous reactors to emphasize the fact that a number of imposing developmental, chemical, and engineering problems exist, and, until these are satisfactorily solved, performance will remain in doubt. To date, the only homogeneous reactor that has been operated is the relatively low-power research reactor at the Los Alamos Scientific Laboratory. As the first major step in investigating and evaluating the problems associated with high-power-density homogeneous reactors, ORNL is proceeding with the design and assembly of the Homogeneous Reactor Experiment (HRE). This experiment is designed primarily to provide information with regard to the design and operating problems of homogeneous reactors in general. It is not intended to provide information as to performance of reactors in achieving any particular objective such as plutonium production. As a matter of fact, the HRE will use highly enriched fuel in the form of a uranyl sulfate dissolved in light water, whereas an efficient plutonium producer would require a solution or slurry in heavy water of natural, or very slightly enriched, uranium. It is anticipated that the HRE will be in operation early in the summer of 1951.

Because a homogeneous reactor containing natural uranium in heavy water would necessarily be quite large, it is probable that the use of slightly enriched uranium would be preferred.

(b) Plutonium Production (Slightly Enriched Uranium. As pointed out, there is nothing sacred about the use of uranium having the isotopic content found in nature as a combined fuel and producer material in converter reactors for the production of plutonium. Large quantities of depleted uranium are available as the result of operation of the gaseous diffusion plants. Also, it is feasible, from the point of view of plant operations, to bleed from the diffusion plants material having almost any desired enrichment. After use in a reactor the material can be fed back into the diffusion plant at a lower point in the enrichment process as determined by the extent of U^{235} burn-up in the reactor. Such combined operations do have their effect on the efficiency of operation of the diffusion plant and on the over-all production of fissionable material. The important point is that one can, in principle, design reactors for operation with a wide range of uranium enrichments and make a selection on the basis of the over-all economics of operations.

Light Water – moderated and – cooled Reactor. A reactor design based on the use of ordinary water as moderator and coolant and using slightly enriched uranium has been developed through phase I by the Atomic Energy Division of the H. K. Ferguson Co. The

DECLASSIFIED

neutron economy of a reactor containing ordinary water as moderator and coolant is not good compared to that in heavy water– or graphite-moderated reactors. However, a light water reactor offers the advantages (1) that most of the external pumping and heat-exchange equipment is standard and (2) the over-all costs of the reactor plant might be considerably less than for other types. Moreover, since there is no necessity for separating the moderator and coolant and since the fuel-rod lattice spacing in light water can be made very close, it appears that highly efficient heat-transfer conditions might be obtained, providing high performance, in terms of plutonium and excess-neutron production, for the capital invested and fuel consumed. This type of reactor also provides an opportunity for simplicity in design. It should be kept in mind, however, that the fuel for such reactors is more costly than natural uranium, and, furthermore, their operation is tied to the operation of a uranium-isotope-separation plant.

In view of the potential advantages of the Ferguson company design, it will be modified to produce power as well as plutonium and neutrons and will be developed through phase II in order to provide an alternate and back-up design to the main line selected by the Du Pont company.

Homogeneous Reactors. Potentially, homogeneous reactors can be applied to the same purposes as heterogeneous reactors. This is true not only for operation in the thermal region but also, if the proper fuels are developed, for operation in the high-intermediate region. The technical and engineering problems associated with the development of homogeneous reactors are quite different from those encountered with heterogeneous reactors. To some persons, homogeneous problems loomed more difficult than heterogeneous problems. That is why today we find ourselves in a world of heterogeneous reactors. Because of this emphasis of past efforts, we are not in a position to evaluate, on the basis of comparable soundness of technical information and experience, the performance of homogeneous reactors against heterogeneous reactors.

With regard particularly to plutonium production, it appears, on the basis of calculations, that the use of slightly enriched-uranium (0.8 per cent) salt or slurry in heavy water would result in better over-all performance than the use of natural uranium. Studies along these lines will be continued at least through phase II.

Modified MTR for Neutron Production. The fuel element developed for the Materials Testing Reactor appears, on the basis of all tests, to satisfy these requirements. In fact, with relatively little redesign the MTR can be modified to operate as an efficient converter reactor for the production of large quantities of neutrons. Such a design modification has been studied by ANL and ORNL through phase II. The design flexibility and efficiency of enriched reactors is not nearly so dependent upon whether heavy water or light water is used as in the case of natural-uranium reactors.

January 1951

011
DECLASSIFIED

The Application of Powder Metallurgy to Problems Involving Beryllium, Zirconium, and Uranium

By B. H. Alexander, H. H. Hausner, and W. E. Kingston

Metallurgical Laboratories
Sylvania Electric Products, Inc.
Bayside, N. Y.

Report SEP-51(X)

ABSTRACT

The advantages of powder metallurgy in certain applications are discussed, and the methods that have been developed for making, pressing, and sintering powders of uranium, beryllium, and zirconium are outlined. Special applications of these methods in the production of fuel elements, in the control of grain size and orientation, in the introduction of discrete particles in a metallic matrix, and in research on phase diagrams, diffusion, homogenization, and alloy development are reviewed.

INTRODUCTION

During the past decade the development and utilization of powder-metallurgy techniques has progressed to a degree where such methods play an important part in the general field of metallurgy. In some respects the properties of material produced by powder metallurgy are not superior to those produced by conventional methods, and it is only in certain cases that it offers unique advantages as compared with standard metallurgical procedures. Some of these advantages are of particular significance to specific problems associated with the AEC programs. As a matter of fact, in many cases powder metallurgy is the only method by which certain technical objectives may be feasibly attained, e.g., the fabrication of metals with controlled porosity.

As its name implies, powder metallurgy is concerned with the forming of dense homogeneous bodies from metal powders. There are many methods by which densification or sintering may be accomplished: cold-pressing the powder into the desired shape, followed by heat-treating or sintering at elevated temperatures; hot-pressing, in which the pressing and sintering operations are carried out simultaneously; and pulse sintering, in which an electric current is passed through the metal powder which is under pressure, thereby heating the powder and resulting in densification. In all cases, however, the principal mechanism involved, that of sintering or homogenization, is essentially a solid-state reaction.

In the cases where it may be employed, powder metallurgy offers one or more of the following advantages:

1. Since the material is always in the solid state, much smaller amounts of impurities are added as compared with techniques involving melting. Thus metals or alloys of higher purity can be made using the same base materials. This is of great importance where the minimization of contamination is a prerequisite, such as in the manufacture of the high melting point metals, tungsten, molybdenum, tantalum, etc.

2. When dies of the proper dimensions are used, parts can be formed to very close tolerances, and

DECLASSIFIED

little or no finishing is required. This results in very small material loss and is particularly important where base materials are costly or are of strategic value. Thus one of the chief advantages of powder-metallurgy processing is the very high efficiency in material utilization.

3. Since the metals are never completely molten, no segregation of lighter or heavier elements results, as would be the case in conventional metal-melting procedures. For example, in the production of alloys of beryllium and uranium or zirconium and uranium for fuel elements, it is important to prevent segregation such as may occur during freezing, and this may readily be done by employing powder-metallurgy methods.

4. Since diffusion is greatly limited in the solid state as compared with the liquid or vapor state, it is possible to incorporate and maintain bodies of predetermined size and composition in a matrix of a different composition or nature.

It is believed that one method of minimizing radiation damage in fuel elements would be to position the active material in the form of particles or masses of discrete size in a matrix of inactive material. By such a method the fission products could damage only a small area in close proximity to the active bodies, leaving the matrix substantially unharmed.

5. Grain size may be controlled by either of two methods. One, which is used for grain-size control in tungsten, involves the addition of insoluble oxides such as ThO_2, which act as inhibitors to grain growth. The other method involves the pressing of the powders at a temperature high enough to allow complete densification but not high enough for grain growth. In the latter method, the grain size is usually equal to or smaller than the particle size of the metal powders. In either method no preferred orientation results.

In connection with dimensional stability of fuel elements, where grain size and degree of preferred orientation have proven to be significant factors, powder-metallurgy techniques have allowed the development of uranium compacts of optimum grain size with an absence of preferred orientation. These have shown a minimum amount of dimensional instability and surface roughening.

One rather unique application of powder metallurgy, which illustrates many of its inherent advantages, is in the preparation of canned uranium slugs. A completely jacketed slug may be made in one operation by hot-pressing uranium powder at 600°C in an aluminum or zirconium can. By this method the completely densified uranium is firmly bonded to the can and the core is composed of randomly oriented fine-grained uranium. The utilization of the expensive uranium is practically 100 per cent, thereby making available considerable savings in scrap and reprocessing. The bond between the uranium and the can is formed without the use of alloy interfaces put on by dipping methods. From a quality standpoint, the matrix, being randomly oriented and of optimum grain size, should be in a most favorable condition for resisting dimensional changes.

The above advantages may be considered as being of prime importance from a standpoint of production or utilization purposes. In addition to these, there are many instances where powder-metallurgy techniques may be used to advantage as a research tool. Several of these aspects will be brought out subsequently. It should be emphasized that powder metallurgy is a specialized technique which has certain inherent advantages, chiefly associated with specific objectives and of particular value where the materials involved are costly or strategic in nature. It cannot compete with conventional methods in the production of large objects of low-cost materials such as iron or copper.

In the following sections we will outline the methods of making and sintering powders of beryllium, uranium, and zirconium and consider some applications in more detail.

THE POWDER METALLURGY OF BERYLLIUM, ZIRCONIUM, AND URANIUM

Powder Preparation

On account of the brittleness of beryllium, mechanical comminution methods can be easily applied for the production of beryllium powders. Vacuum-cast beryllium billets are chipped, and the chips are ground in an attrition mill in an atmosphere of purified nitrogen. During the grinding procedure the material picks up some oxygen, and the amount of the oxygen determines the quality of the powder. Beryllium powder used for powder-metallurgy purposes usually contains 1 per cent BeO or more. The powder leaving the attrition mill passes a 200-mesh screen, and the particles vary in size from approximately 1 to 74 μ. Many of the larger particles, however, are agglomerates of smaller particles which break up during pressing.

Zirconium and uranium are very ductile and do not, therefore, permit mechanical comminution. Both metals, however, form hydrides when they are heated in a hydrogen atmosphere. The brittle hydrides can be ground to powders and decomposed to the respective metals. Zirconium hydride (ZrH_2) is formed at approximately 800°C and uranium hydride (UH_3) at approximately 250°C. The ZrH_2 powder particle size can be controlled by the degree of mechanical comminution, whereas UH_3, as formed, is so fine that no grinding is required. It seems that the fine particle size of UH_3 is characteristic of its formation, and little change in size can be obtained by varying the method of formation of the hydride. The average particle size of the uranium powder is about 0.5 μ.

714 013
DECLASSIFIED

The powder contains a large fraction of particles as fine as 0.1 μ and many larger particles which were usually found to be agglomerates of fine particles as shown in the electron micrograph (Fig. 1). We have made spherical uranium powders of larger particle size by atomizing liquid uranium.

Uranium, zirconium, and beryllium powders are extremely reactive in air and precautions must be taken in their storage and handling to prevent contamination. Precautions must also be taken from a safety and health standpoint.

Pressing

Although many factors can influence the pressing behavior of metal powders, usually the most important factor is the compacting pressure, and it is important to determine its effect on the pressed density and sintering behavior.

Figure 2 shows the effect of compacting pressure on the density of the pressed compact for powders of uranium, zirconium, and beryllium. The density of a pressed compact, however, is not exclusively a function of the material and of the compacting pressure but also depends on the size and shape of the part, or more specifically, on the ratio of the pressing area to the area of the compact which is in contact with the die walls (wall area). Because of the smaller die wall friction, thin samples can be pressed with a lower compacting pressure than samples having the same pressing area but greater height.

The compacting of ordinary metals such as copper and nickel is usually done in air. Uranium powder, however, must be compacted in a protective atmosphere such as argon. In order to avoid oxidation, beryllium also should be handled in an inert atmosphere. Zirconium and zirconium hydride powders can be pressed in either air or argon with no apparent differences, although the inert atmosphere is used to avoid contamination.

Sintering

As might be expected, the extent of sintering or densification and most of the physical properties of the sintered compact are strongly affected by the sintering temperature, time, and atmosphere.

The sintering atmosphere is chosen to prevent undesired reactions and consequent contamination or to promote the reduction of surface oxides, removal of adsorbed gases, etc. It was found that beryllium, zirconium, and uranium are advantageously sintered in vacuum.

The effect of sintering temperature on the density of the sintered compacts of these metals is shown in Fig. 3, where a curve for nickel is shown for comparison.

Zirconium-metal powder compacted at 50 tons/sq in. sinters to its theoretical density at a temperature of approximately 70 per cent of the melting temperature of zirconium, whereas uranium and beryllium do not sinter effectively until the temperature is about 90 per cent of their melting temperatures. It is interesting to note that pressed ZrH_2 powder sinters to dense zirconium metal at a temperature slightly lower than that required for zirconium powder. It seems that the formation of the metal by decomposition of the hydride during the sintering heat treatment increases the reactivity of the material and facilitates sintering. Besides the ease in sintering, ZrH_2 powder has the advantage of being easier and cheaper to manufacture than zirconium powder, and, furthermore, it is less pyrophoric.

The grain growth that accompanies sintering is shown in Fig. 4 for beryllium and in Fig. 5 for zirconium. Beryllium powder compacts can be sintered in argon or in vacuum, although there is a substantial difference in the results obtained by sintering in these two atmospheres. Grain growth is slightly less in vacuum than in argon. Figure 6 shows a comparison of a beryllium compact sintered at 1220°C for 3 hr in vacuum and in argon. Besides this difference in grain size, it was found that beryllium compacts sintered in argon are extremely brittle, whereas vacuum-sintered beryllium compacts show some indications of ductility. The latter could be cold-rolled 8 to 10 per cent without cracking and then, after annealing, could be further reduced a similar amount.

Uranium powder, as produced by the hydride method, never densifies to more than 92 to 93 per cent of the theoretical density when ordinary pressing and sintering is applied. Repressing the sintered specimen at pressures as high as 100 to 150 tons/sq in. increases the density slightly but never leads to a completely dense material. In order to obtain a completely dense uranium by powder-metallurgy methods, the hot-pressing technique is employed. The densification of uranium during ordinary sintering takes place in the gamma range, and the resulting material has a very coarse grain size (Fig. 7).

The Powder Metallurgy of Materials with Two or More Components

The powder-metallurgy preparation of a zirconium-uranium alloy may be given as an example of compacting and sintering of two alloying components. Alloys of this type containing high percentages of uranium cannot be made easily by ordinary melting. Mixing uranium and zirconium or uranium and ZrH_2 powders results in a uniform dispersion with no segregation during pressing. Heating these compacted mixtures results in homogenization and densification. Figure 8 shows sixteen microphotographs of a com-

DECLASSIFIED

pacted mixture of zirconium plus 1 wt. % uranium pressed at 50 tons/sq in. and sintered at various temperatures and times. The process of homogenization can be followed easily.

The powder-metallurgy method of pressing and sintering mixtures of two or more components which do not form an alloy can be applied to metals and also to mixtures of metals and nonmetals. The method of pressing and sintering nonalloying metals has been used for several years for the production of the so-called "compound metals" which are used for electrical contacts. Figure 9 shows a compound metal consisting of a mixture of molybdenum and silver. This mixture, when sintered, combines the good wear resistance of molybdenum with the good electrical conductivity of silver. The same method can be applied in the production of materials which consist of discrete particles of some metal or metal compounds in a matrix of another metal. Figure 10 shows a microphotograph of a pressed and sintered mixture of uranium carbide particles and zirconium powder. The carbide, after sintering, remains in the form of discrete particles in the zirconium matrix.

Hot Pressing

The two processes, described above, of pressing and sintering can be done in a single operation which is called hot-pressing. Hot-pressing of beryllium powder produces a nonporous beryllium, although this material is brittle (Fig. 11). Hot-pressing of zirconium powder is easily accomplished (Fig. 12), although it offers no improvement in properties over the two-stage pressing and sintering described above. Hot-pressing of uranium in the alpha range results in a dense material of small, randomly oriented grains (Fig. 13). Uranium powder made by the hydride method is used for this purpose; it is compacted at a pressure of approximately 30 tons/sq in. and at a temperature between 600 and 660°C.

SOME APPLICATIONS OF POWDER METALLURGY OF INTEREST TO THE AEC

In the following section, some of the problems of interest to the AEC which are now being investigated in the Metallurgical Laboratories at Sylvania using the powder method will be described.

Production of Fuel Elements

The principal reason for attempting to develop powder-metallurgical methods of producing fuel elements is that there are possible economies to be gained over the methods currently used. We have successfully produced plate-type elements of zirconium-uranium alloys in a sheath of zirconium by first pressing the zirconium-uranium alloy powder into the desired shape and subsequently pressing a zirconium powder cladding onto this. [A new die has recently been completed which will simplify this operation (Fig. 14).] The sandwich is then sintered, and a good alloy bond is formed at the zirconium-uranium interface (Fig. 15). These specimens are currently being given further tests to determine their ability to withstand damage due to radiation and thermal cycling.

We are also attempting to develop methods of making Hanford type fuel elements in a one-stage operation by hot-pressing uranium powder into zirconium or aluminum cans at 600°C. This results in a uranium structure that should be ideal from the standpoint of dimensional changes and should allow appreciable economies in manufacture. The aluminum can is deformed slightly by pressing at 600°C, and the bond is, in fact, too good, for uranium actually penetrates to the outside of the aluminum can. This excessive diffusion can be minimized by anodizing the inside of the aluminum can. An excellent bond, with very little diffusion, is obtained by hot-pressing uranium powder onto zirconium (Fig. 16).

Introduction of Discrete Particles

In a study being made by the Westinghouse physics group on the range of damage of fission products, it was desired to introduce U^{235} particles in a matrix of U^{238} or zirconium. For this purpose, it was first necessary to make the U^{235} in the form of a compound which would not decompose during the sintering of the matrix. After investigating several compounds it was found that UC and UN were stable in a zirconium matrix (Fig. 10) but that UN, UO_2, and UC were not sufficiently stable in a uranium matrix to withstand high-temperature sintering. However, any of these compounds are stable in a uranium matrix which is hot-pressed at 600°C.

It is certainly feasible to introduce metallic particles of U^{235} into a matrix of U^{238} and to avoid extensive interdiffusion by using the hot-pressing technique.

This is an ideal example of some of the unusual combinations, obtainable by using powdered metals, that cannot be obtained by other methods of fabrication.

Control of Grain Size and Orientation of Uranium

We have spent considerable effort in developing a fine-grained uranium with random orientation. Such material should exhibit little or no dimensional change on thermal cycling. In these studies we initially followed the techniques that have proven successful in controlling grain growth in tungsten, i.e., the addition of a small amount of insoluble impurity which would form a grain-boundary film and thus inhibit grain growth. Uranium powder was coated with several dif-

C15

DECLASSIFIED

ferent oxides before compacting and sintering. Although some grain refinement was obtained, it was inadequate. Presumably the high sintering temperatures required resulted either in the decomposition or dissolution of the added oxides, so that they were no longer effective in restricting grain growth. An example of the effect of ThO_2 in uranium is shown in Fig. 17.

We have abandoned these attempts upon finding that a fine-grained, randomly oriented uranium can be readily produced by hot-pressing uranium powder in the alpha range at 600°C. (The small deformations involved in pressing metal powders do not result in any marked preferred orientation.) The low temperature and short time involved in this operation did not cause grain growth, as can be seen in Fig. 13. Upon thermal cycling in the alpha range, this material retains a smooth surface and undergoes little dimensional change.

The Use of Powder Metallurgy as a Research Tool

There are many research problems involving studies of the constitution of alloys, grain growth, reactions in the solid state, diffusion, and homogenization that can be attacked conveniently by using powdered metals. The use of powder metallurgy in research on structure-sensitive properties has certainly not been explored adequately. The wide variety of structural variations and the control over them that can be had by using powdered metals and alloys makes it far superior to other methods of sample preparation for this kind of study.

Phase Diagrams. The difficulty of avoiding contamination from the atmosphere and crucible while melting alloys of zirconium and beryllium, for example, has been avoided in a preliminary study we have made of the phase diagram of this binary system. The alloy specimens were made using the zirconium and beryllium powders obtained by the methods described in the last section. The small size of these powder particles led to rapid homogenization upon heating for short times at temperatures higher than about 700°C. By selecting ten different compositions and annealing each at three different temperatures, the principal features of the zirconium-beryllium phase diagram were determined. By making specimens from powders, we could obtain much more uniform and accurate concentrations in less time than by melting. The microstructures of some of these alloys are shown in Fig. 18. There are many other phase diagrams involving zirconium, beryllium, and uranium that could be more conveniently studied by this method than by any other. The ease of making specimens suggests that further work be done not only on binary systems but on ternary and polynary systems using this method.

Diffusion. It has been demonstrated in this laboratory that the rates of self-diffusion in solids may be obtained from measurements of the rates of sintering of metal powders. A convenient method of making such studies is to make specimens from closely packed spherical powder particles or, more readily, from closely wound wire specimens. An example of the changes that occur on heating the latter type of specimen is shown in Fig. 19. We have found that the rate of sintering in such specimens is directly proportional to the rate of self-diffusion of the metal. Studies of this kind are providing much information concerning the mechanism of sintering itself. When these specimens are made by alternately winding layers of dissimilar metals, their relative rates of sintering are clearly demonstrated, as can be seen in Fig. 20. Such studies show that when a mixture of two different metal powders is sintered, the bonding is almost exclusively due to the one with the higher rate of self-diffusion.

It is convenient in some measurements of interdiffusion of different metals to use one in the form of a powder, e.g., by embedding solid copper in brass powder, a constant zinc concentration can be maintained at the surface of the copper by volatilization of zinc from the brass powder. This method avoids the necessity of forming a welded interface as is customary in making specimens for the measurement of intermetallic diffusion. In this way we are studying the diffusion of zinc into copper single crystals (Fig. 21). The dimensional changes that accompany diffusion are also being investigated by studying the bonds formed between dissimilar metal particles (Fig. 22).

Homogenization. The use of powder mixtures is about the only way that specimens can be made that will be suitable for quantitative studies of the rate of homogenization where it is necessary to have a predetermined concentration distribution. An example of a qualitative study of homogenization in a uranium-zirconium alloy is shown in Fig. 8. This could be done quantitatively by starting with uniformly sized powders and by measuring property changes such as hardness or resistivity as a function of homogenization time.

Alloy Development. Powder metallurgy is a most convenient method of adding highly volatile elements such as zinc or magnesium to a base metal having a high melting point. Although we have only made preliminary attempts to make some alloys of this type, e.g., zirconium and magnesium (Fig. 23) and zirconium-beryllium-uranium (Fig. 24), it may prove profitable to investigate more thoroughly the properties of

DECLASSIFIED

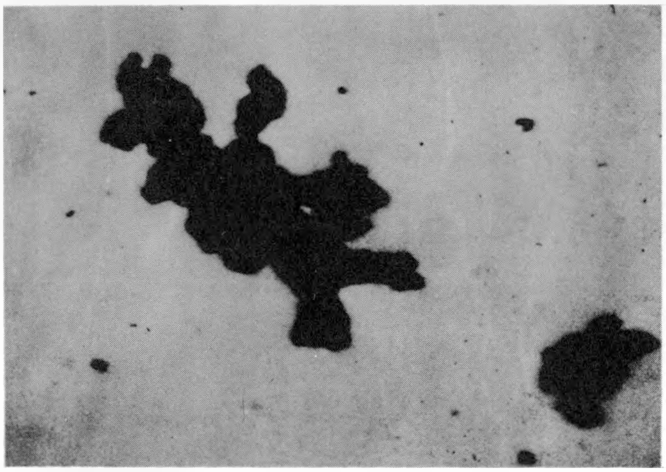


Fig. 1 — Electron micrograph (10,000 ×) of uranium powder produced by the hydride process. It can be seen that most of the particles are smaller than 1 μ and that there is a tendency for agglomeration.

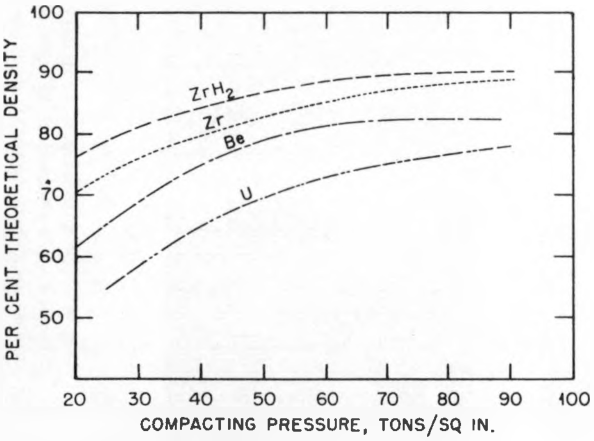


Fig. 2 — The effect of compacting pressure on the density of powders of uranium, beryllium, zirconium, and ZrH_2. For good sintering behavior it is neither necessary nor desirable to use pressures in excess of about 50 tons/sq in.

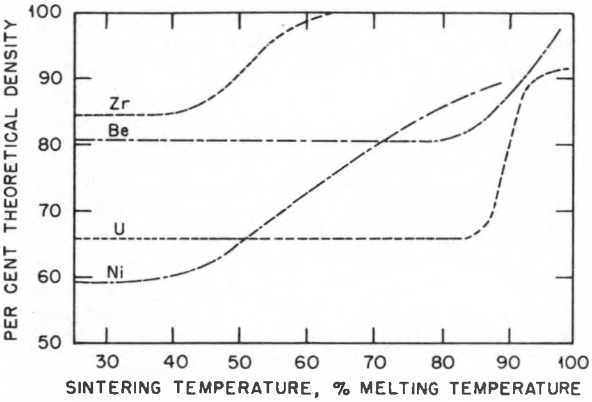


Fig. 3 — The effect of sintering temperature on the density of compacts which have been pressed at 50 tons/sq in. Notice that zirconium sinters to its maximum density at a relatively low temperature compared to beryllium and uranium.

Metal	Compact pressure, tons/sq in.	Sintering time, hr	Remarks
Zr	50	3	ZrH_2 powder used
Be	50	3	Mechanically comminuted Be
U	50	3	Made by the hydride method
Ni		2	Carbonyl nickel

DECLASSIFIED

DECLASSIFIED

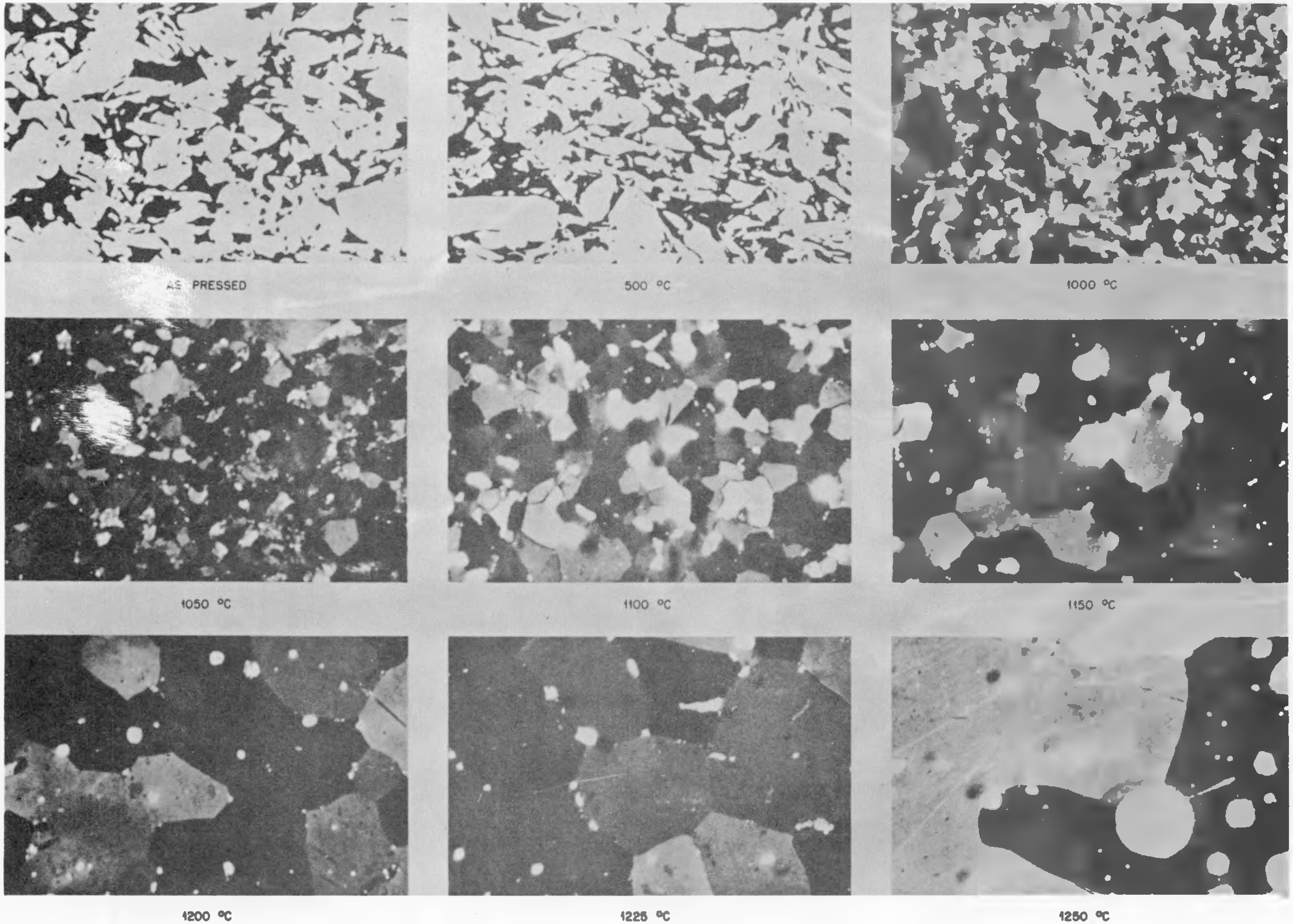


Fig. 4 — The microstructures of beryllium compacts after various sintering treatments. The powders were pressed at 50 tons/sq in. and sintered in argon for half an hour. The white areas, which become spherical at the higher temperature, are BeO. (Magnification 250×.)

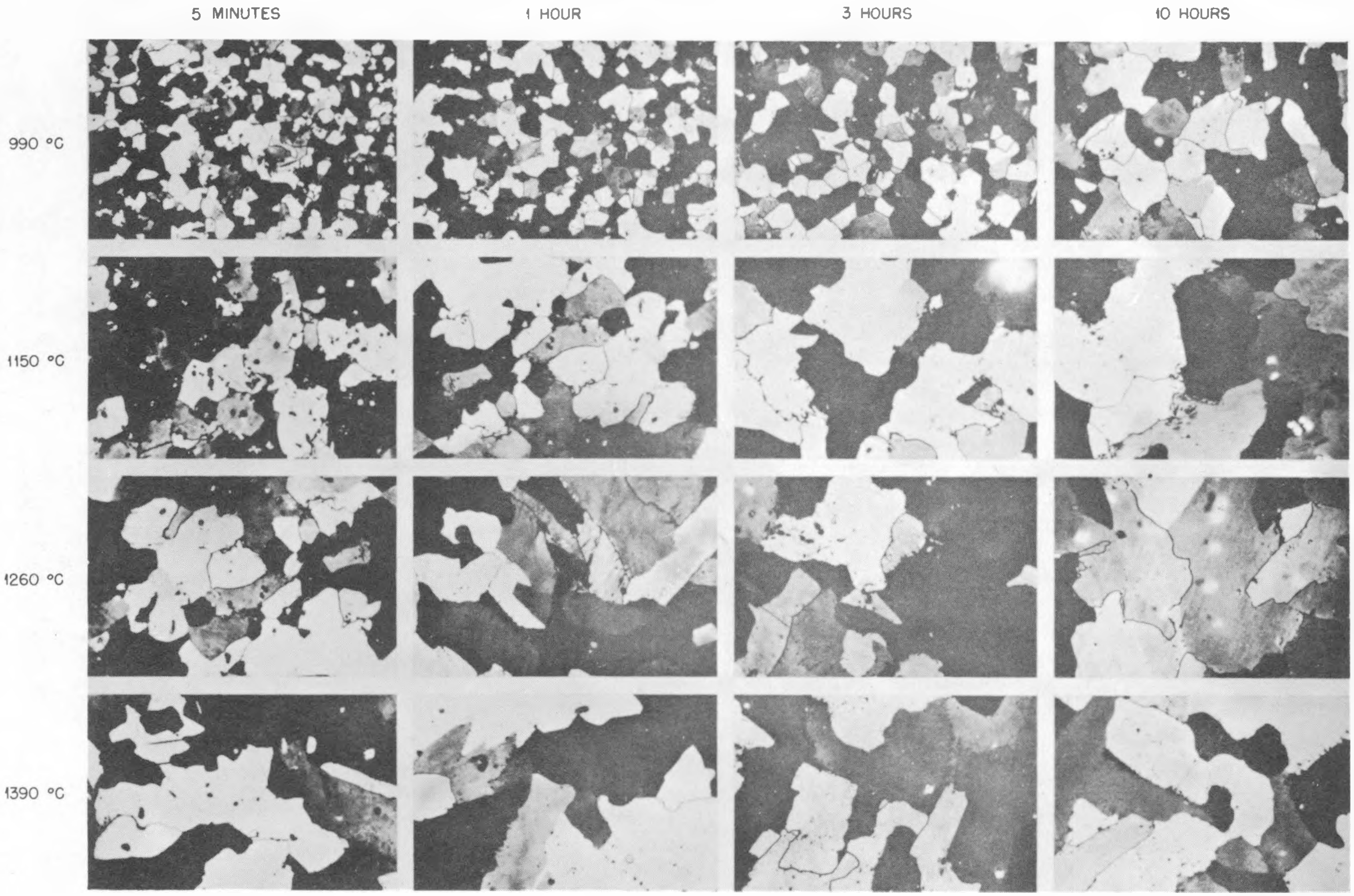


Fig. 5—The effect of sintering time and temperature on the grain growth of zirconium. Compacts pressed at 50 tons/sq in. from −325 mesh zirconium hydride powder and sintered in vacuum. (Magnification 250×, reproduction reduced one half.)

714
C19

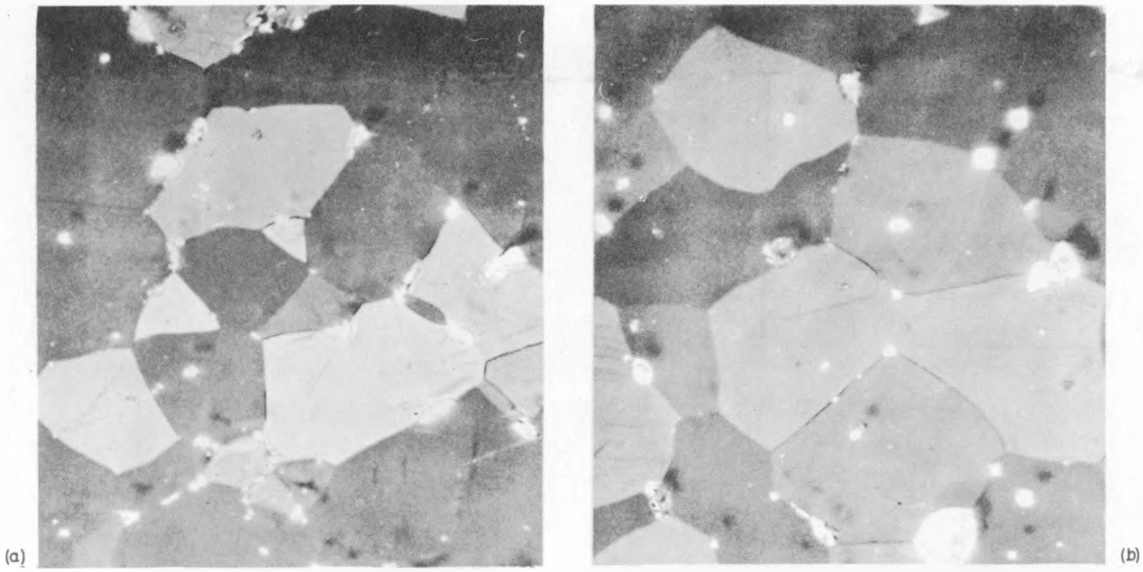


Fig. 6 — A comparison of the structures of **beryllium** sintered (a) in vacuum and (b) in argon. In each case the specimens were sintered for 3 hr at 1220°C. A slightly larger grain size results upon sintering in argon, although the vacuum-sintered specimen was slightly ductile. (Magnification 250 ×.)

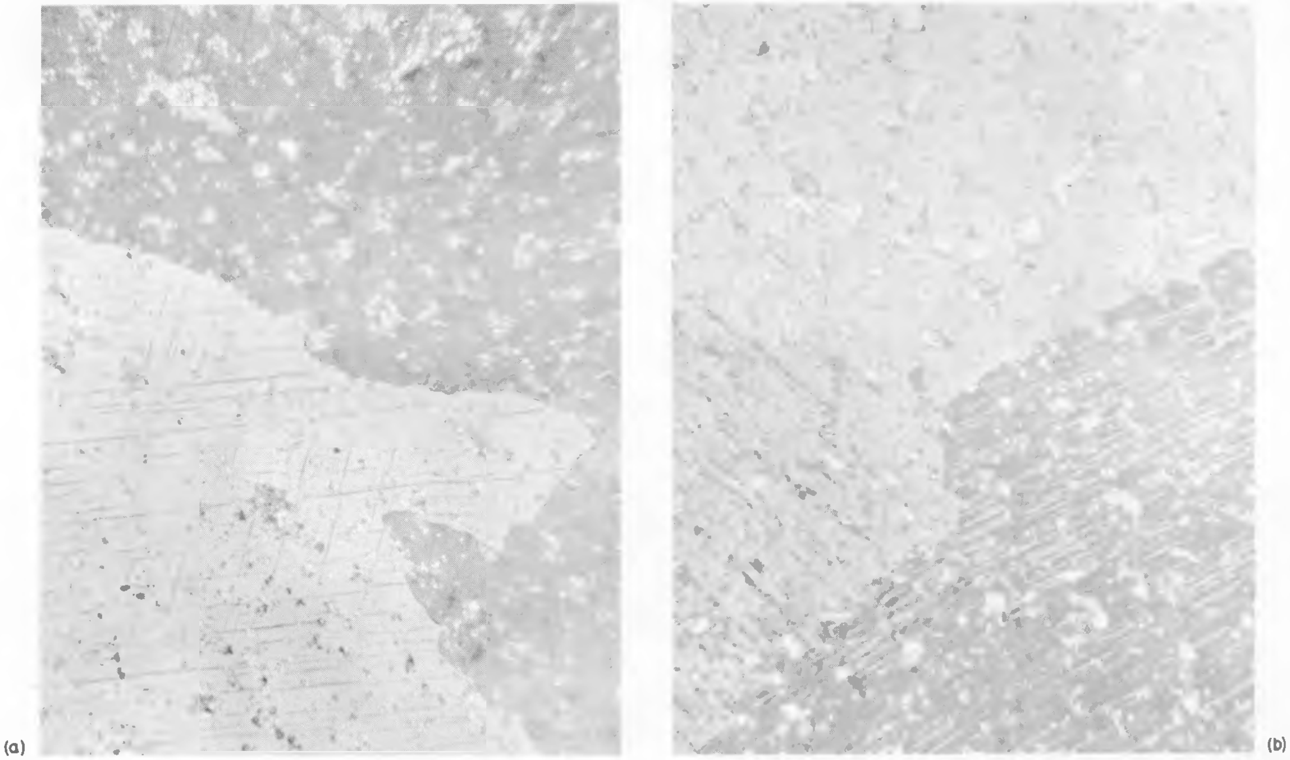


Fig. 7 — (a) The specimen has been pressed at 70 tons/sq in. and sintered 3 hr at 1090°C. The density is about 91 per cent of the theoretical density of uranium. (b) The specimen had received the same treatment as (a) and was subsequently repressed at 140 tons/sq in. and annealed for 1 hr at 500°C. This resulted in a slight increase in density. (Magnification 200 ×.)

714 020

DECLASSIFIED

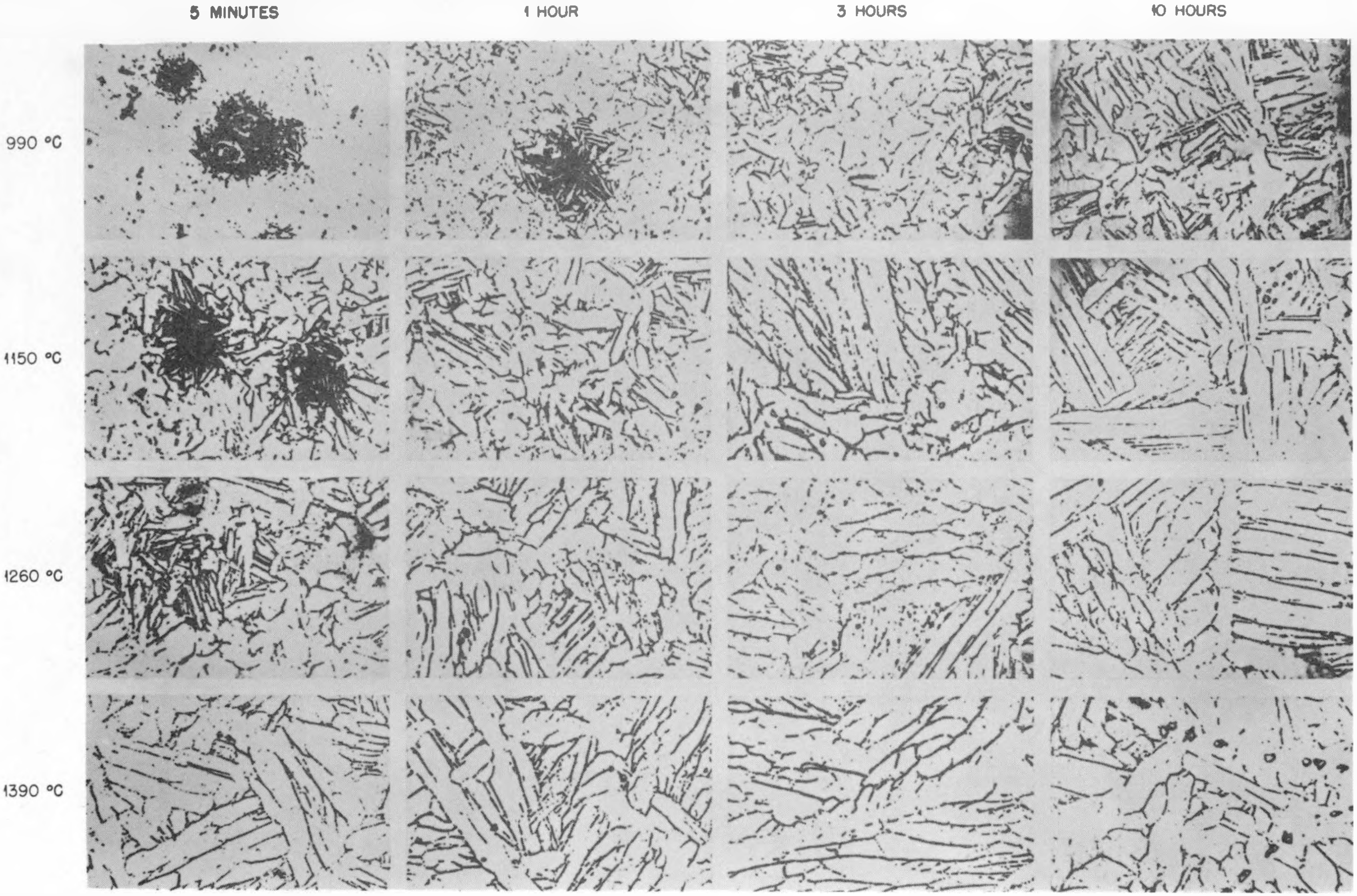


Fig. 8—The effect of sintering time and temperature on the microstructure of 1 per cent uranium-zirconium alloys. Compacts pressed at 50 tons/sq in. from a mixture of −325 mesh zirconium hydride and −325 mesh uranium powders and sintered in vacuum. (Magnification 250×, reproduction reduced one half.)

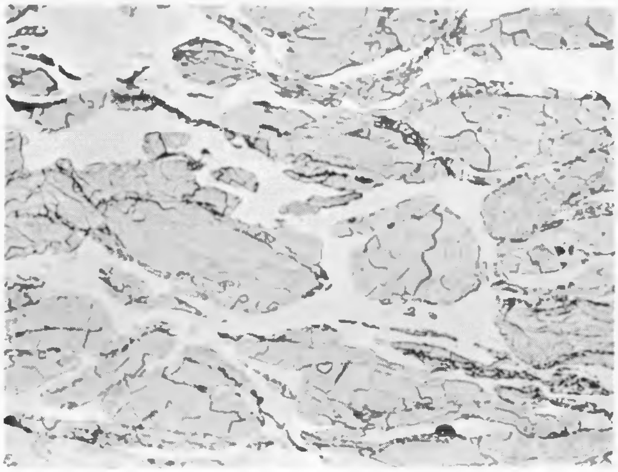


Fig. 9—Microstructure of a mixture of molybdenum and silver powders which were pressed at 30 tons/sq in. and sintered for 2 hr at 920°C. (Magnification 200×.)

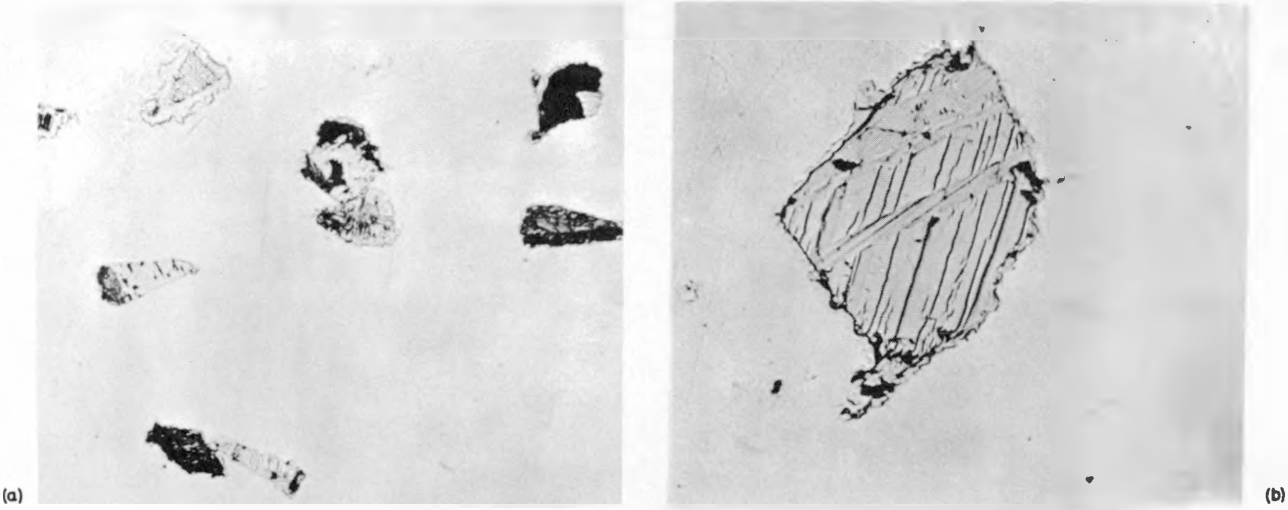


Fig. 10—Dispersion of UC particles in a zirconium matrix. Pressed at 80 tons/sq in. and sintered 10 min at 1200°C in vacuum. Microchemical analysis has shown that no uranium has diffused more than a few microns into the zirconium matrix. (a) Magnified 100×. (b) Magnified 350×.

DECLASSIFIED

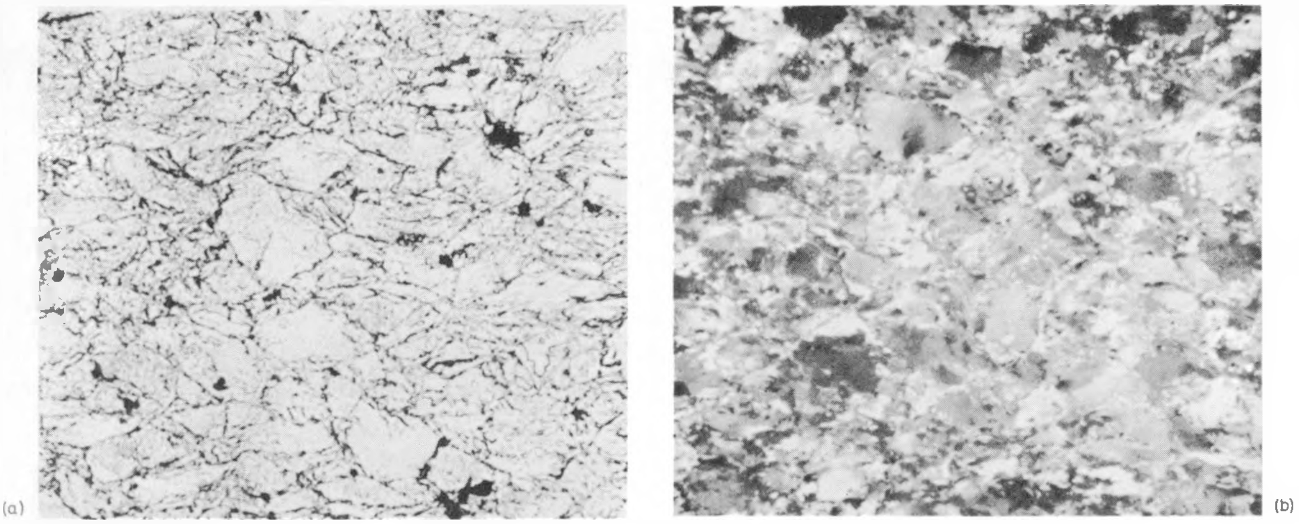


Fig. 11 — Microstructure of beryllium powder hot-pressed at 600°C for 15 min at 25 tons/sq in. (Magnification 250 ×.) (a) Bright field. (b) Polarized.

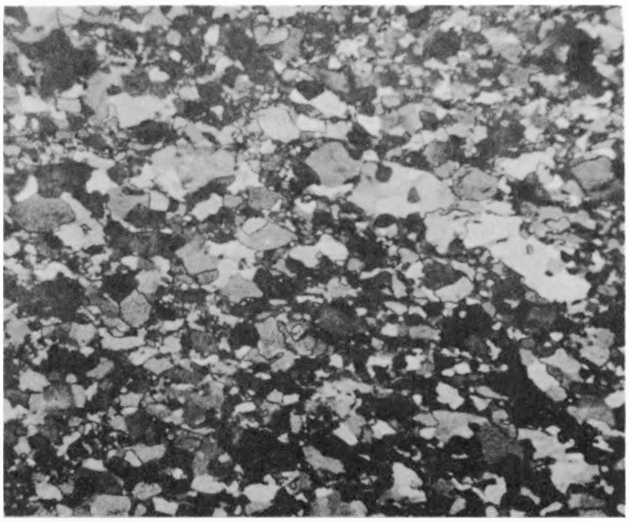


Fig. 12 — Microstructure of zirconium powder hot-pressed at 600°C for 15 min at 25 tons/sq in. (Magnification 250 ×.)

714 C23

DECLASSIFIED

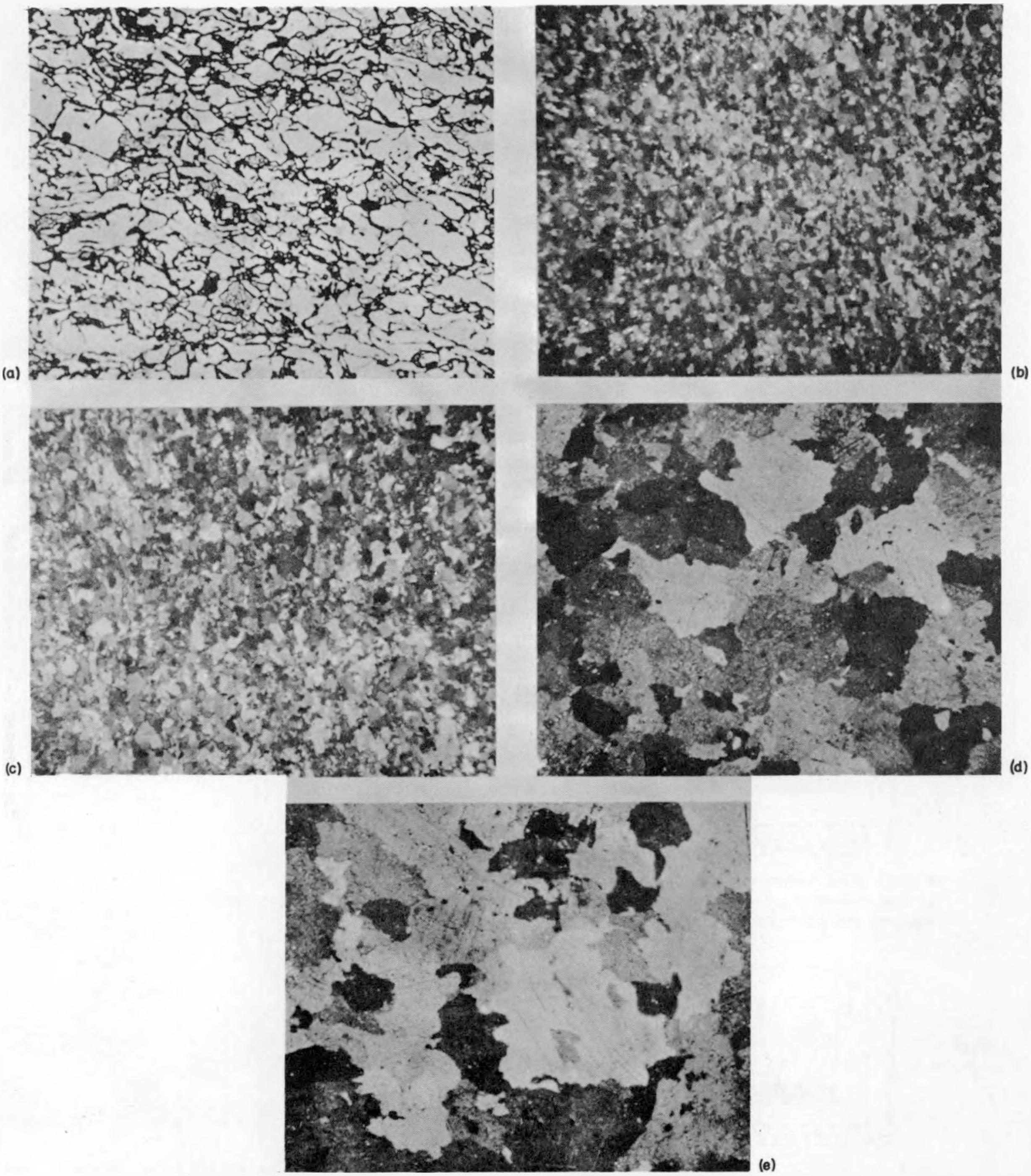
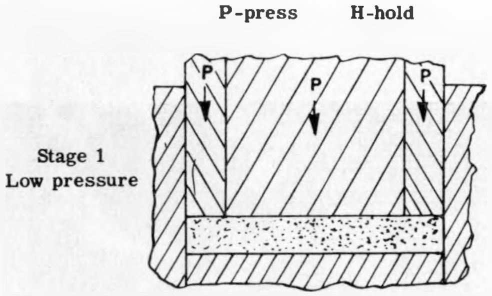
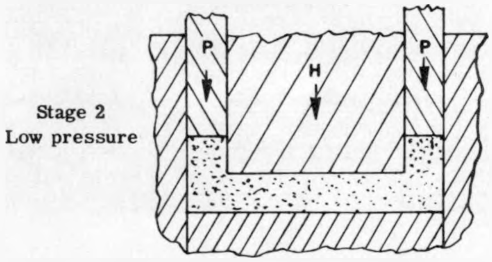


Fig. 13—The structure of uranium powder hot-pressed at 600°C, 25 tons/sq in., for 15 min. The density of this material is 18.77 g/cc. (a) Bright field, as pressed. (Magnification 500×.) (b) Polarized light, as pressed. (Magnification 200×.) (c) Polarized light, annealed 10 sec at 680°C after pressing. (Magnification 200×.) (d) Polarized light, annealed 100 sec at 680°C after pressing. (Magnification 200×.) (e) Polarized light, annealed 1000 sec at 680°C after pressing. (Magnification 200×.) It can be seen that the fine grained material obtained by hot-pressing in the alpha range (b) attains a much larger grain size after a short time anneal in the beta range (d) and (e).

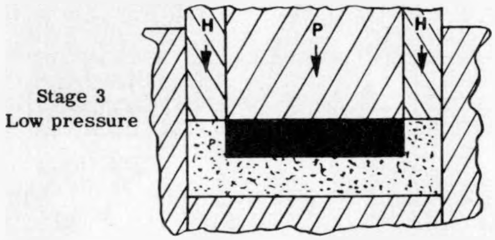
DECLASSIFIED



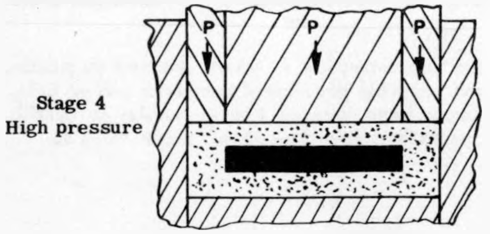
Die is filled with zirconium hydride powder and two-piece multiple plunger moves down together to press lower layer.



Inner plunger remains in place, picture frame plunger is lifted, zirconium hydride powder placed in picture frame cavity, and picture frame plunger presses perimeter.



Picture frame plunger remains in place, zirconium hydride-uranium mixture powder inserted and inner plunger presses core.



Both plungers move up, die is filled with zirconium hydride powder, both plungers move down simultaneously and press top layer.

Fig. 14—Schematic representation of the pressing operation in the production of fuel-element sandwiches.

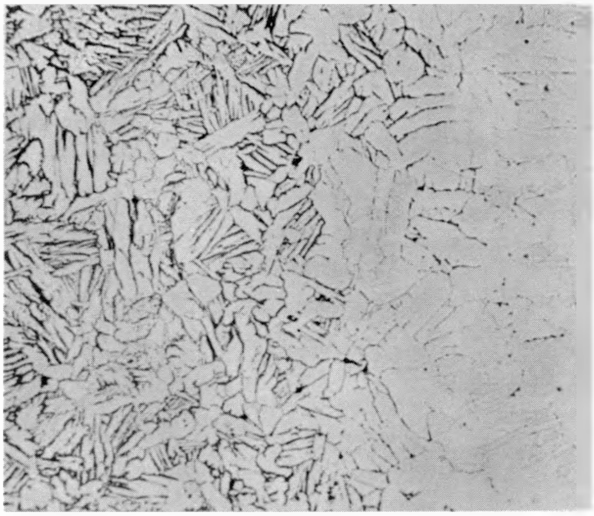


Fig. 15—Microstructure of the bond formed between a zirconium-10 per cent uranium core and a pure zirconium clad. The powders were pressed at 60 tons/sq in. and sintered 3 hr at 1260°C in vacuum. (Magnification 100×.) There is no evidence of the original interface, and a perfect diffusion bond has formed.

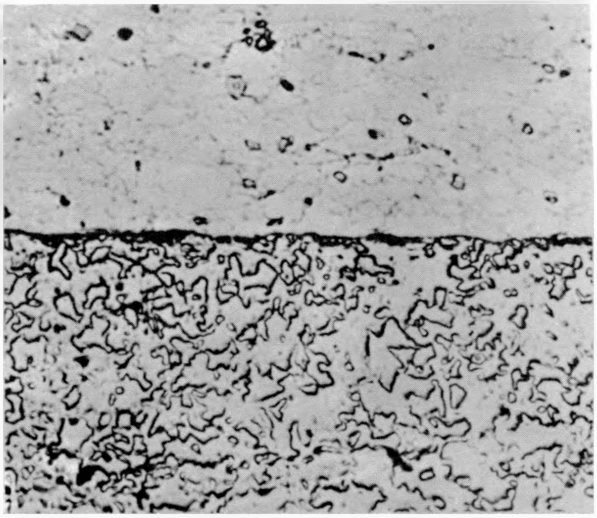


Fig. 16—Microstructure of the bond formed between pure zirconium and pure uranium by hot-pressing the powders for 15 min at 600°C and 25 tons/sq in. (Magnification 500×.)

C25

DECLASSIFIED

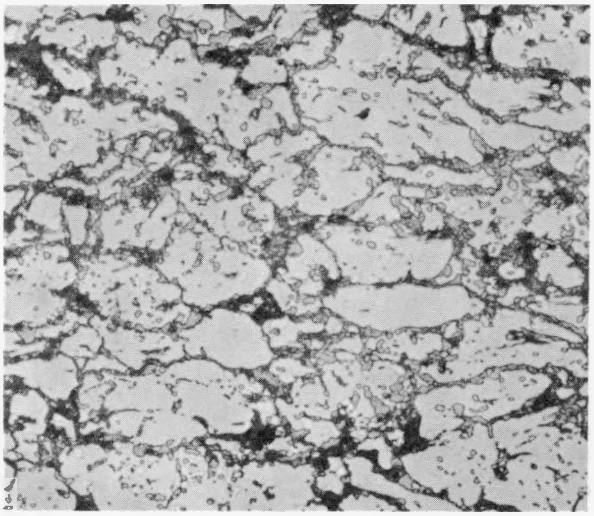


Fig. 17—Microstructure of uranium powder which has been pressed and sintered after the addition of 0.02 per cent ThO_2. By comparing the grain size here with that shown in Fig. 7, it can be seen that the addition of ThO_2 resulted in a somewhat smaller grain size. (Magnification 200×.)

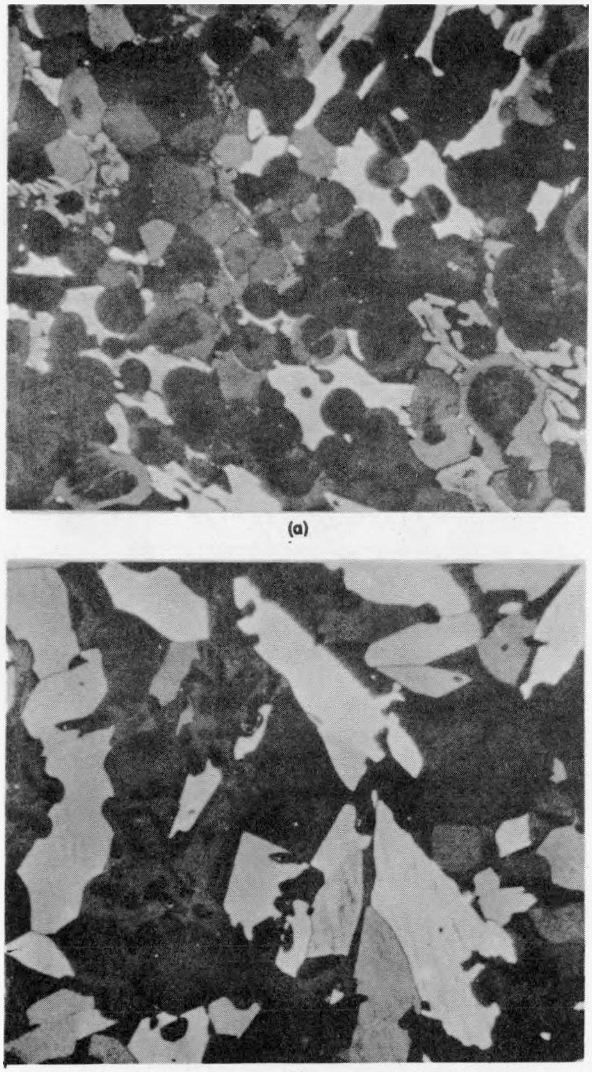


Fig. 18—The microstructure of alloys obtained by mixing, pressing, and sintering powders of beryllium and of ZrH_2. These specimens were sintered 2 hr in vacuum at 1100°C. (Magnification 200×.) (a) 90 Zr–10 Be. (b) 98 Zr–2 Be.

DECLASSIFIED

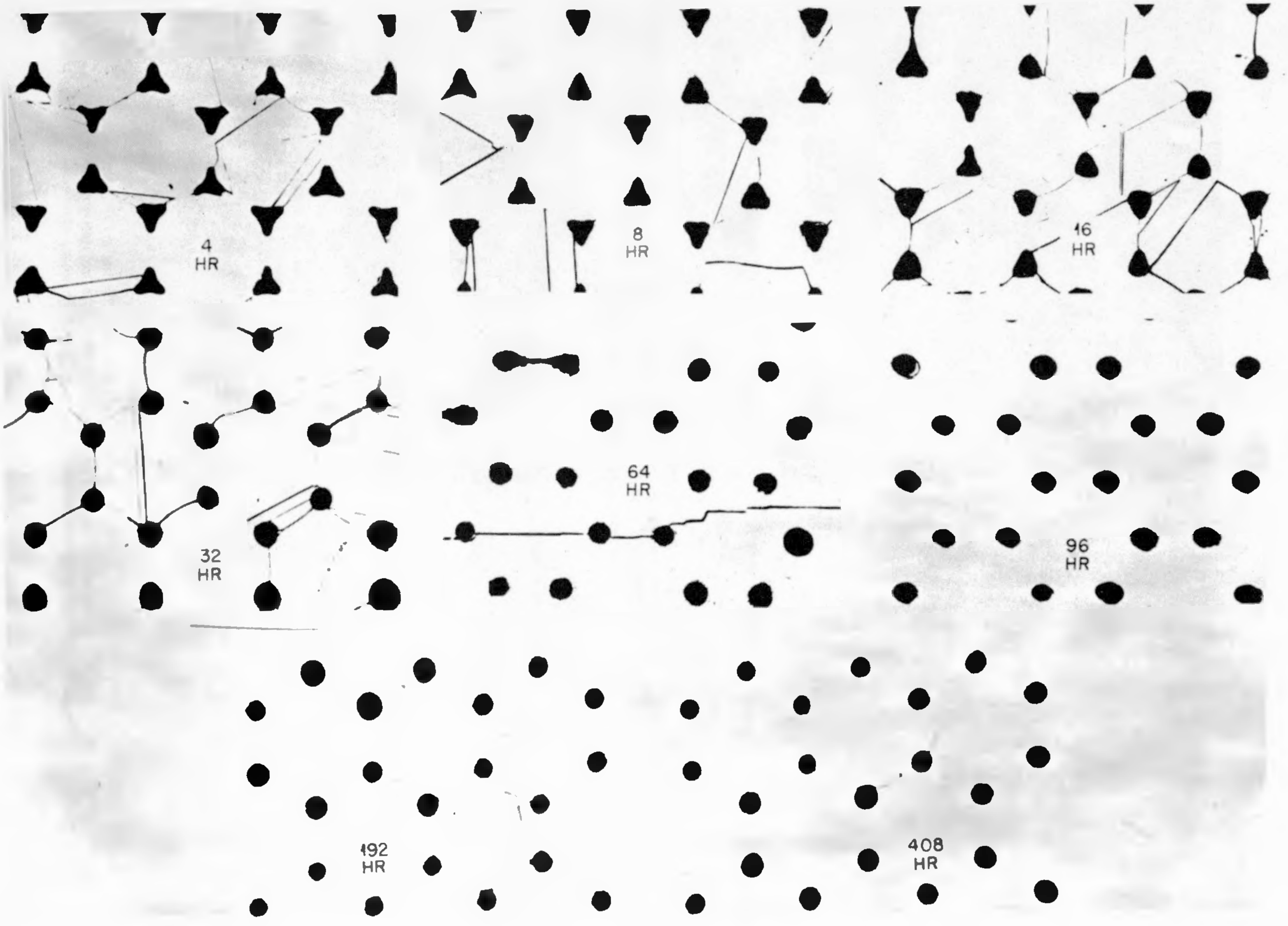


Fig. 19—Cross section of a bundle of 5-mil copper wires after sintering for various times at 1075°C. The change in size and shape of the voids shows the progress of sintering. (Magnification 200 ×, reproduction reduced one fourth.)

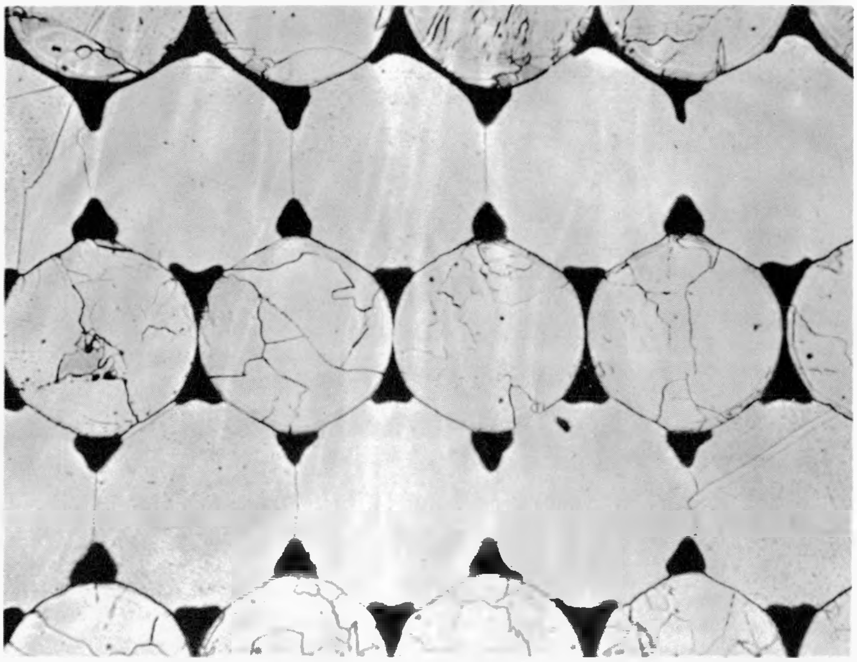


Fig. 20—Cross section of a bundle of alternate layers of 5-mil copper and iron wires after sintering 48 hr at 1000°C. Note that the bonds formed between adjacent copper and copper, and copper and iron wires are approximately equal, while the bond formed between iron and iron is very small or nonexistent after this treatment. (Magnification 200×.)

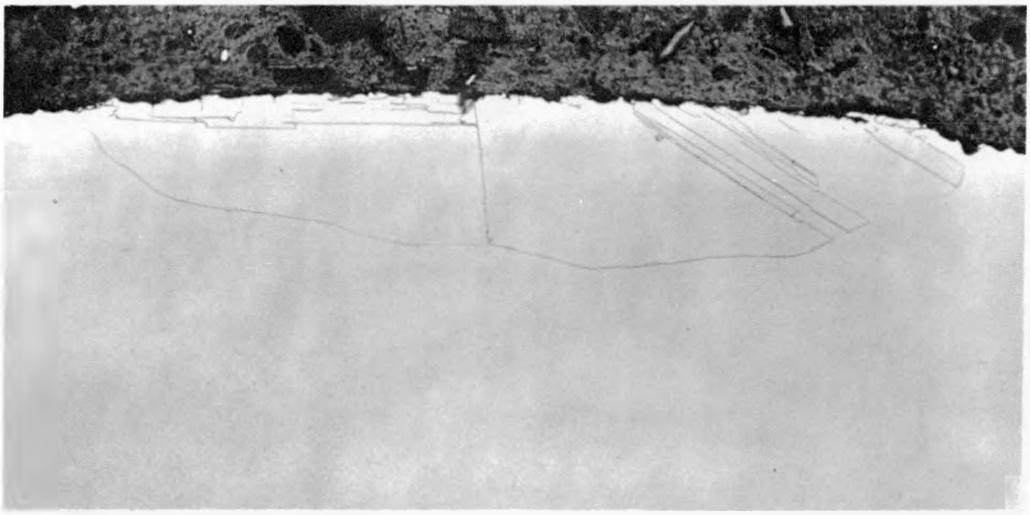


Fig. 21—The surface of a copper single crystal which has been heated in an atmosphere of brass powder 16 hr at 865°C. The diffusion of zinc into the copper has set up stresses resulting in recrystallization. (Magnification 200×.)

DECLASSIFIED

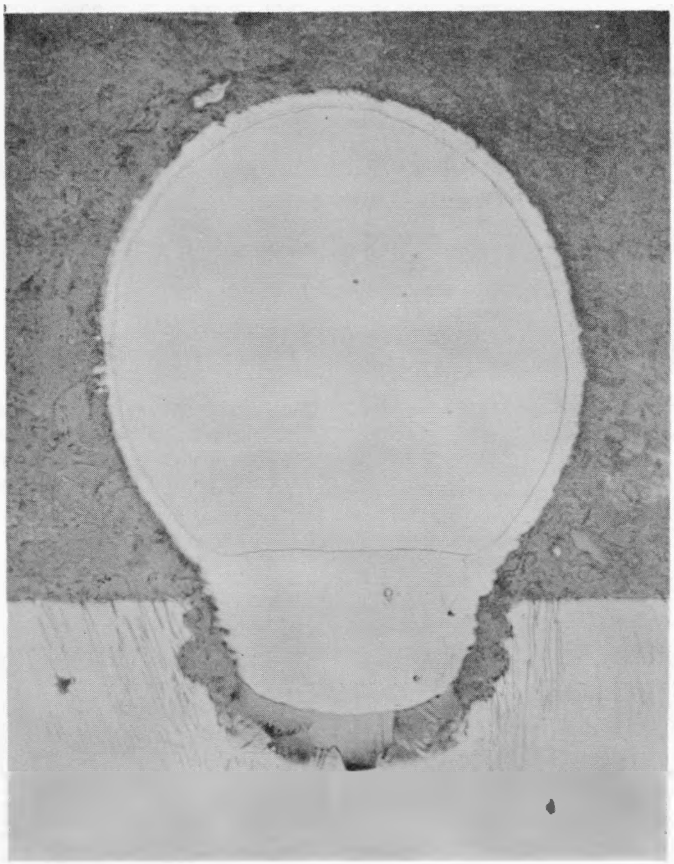


Fig. 22 — Micrograph showing the cross section of a 10-mil copper wire in contact with a pure zinc surface after heating 1 hr at 367°C. (Magnification 250 ×.) Note the formation of intermediate phases and, especially, the grooves formed in the zinc surface.

C29

714

DECLASSIFIED

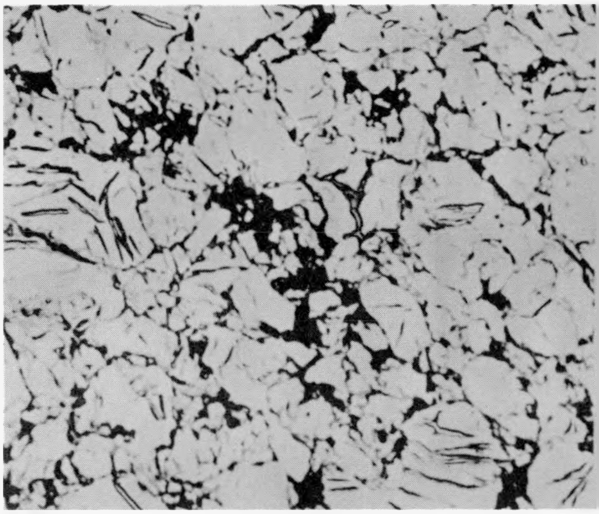


Fig. 23—The structure of a 90 per cent Zr–10 atomic per cent Mg alloy formed by powder metallurgical methods. (Magnification 200×.)

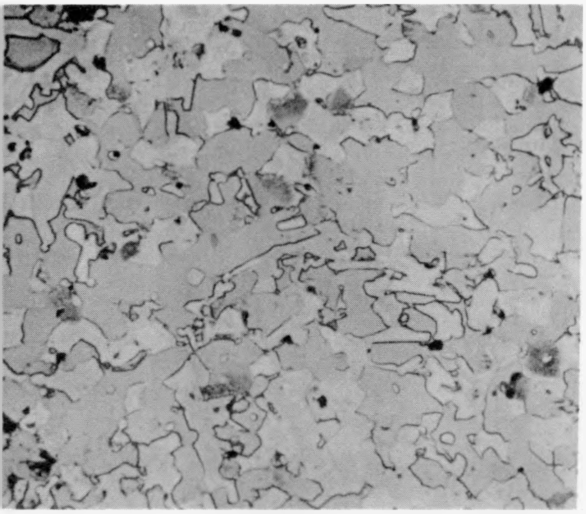


Fig. 24—A ternary alloy consisting of approximately 15 per cent uranium, 15 per cent beryllium, and 70 per cent zirconium, formed by sintering a pressed mixture of the powders 2 hr at 1100°C. (Magnification 200×.)

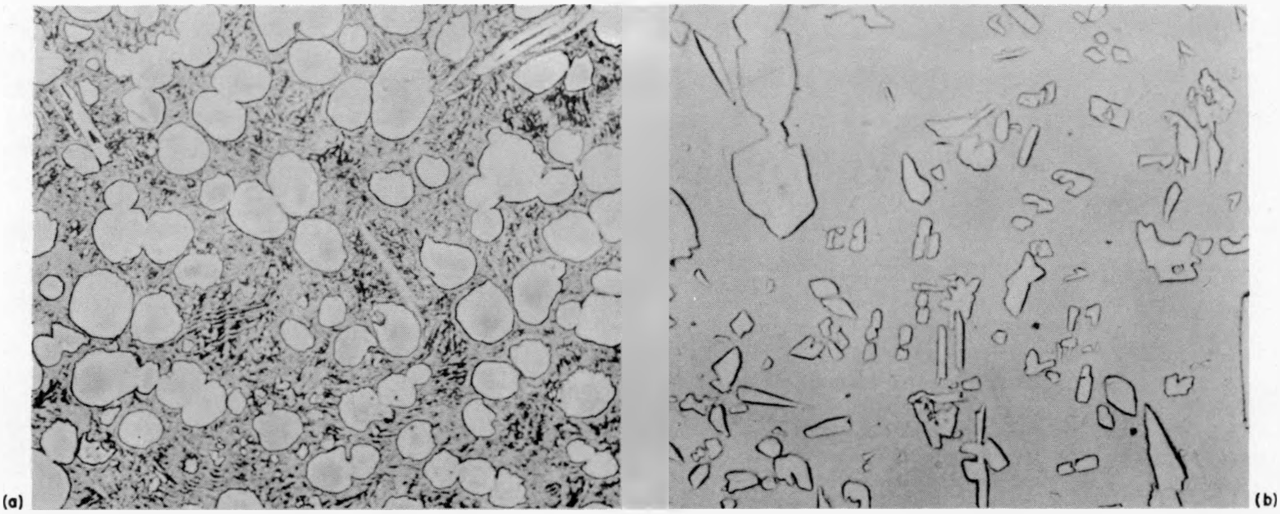


Fig. 25—Microstructures of some zirconium-uranium alloys formed by powder metallurgical methods. (Magnification 350×.) (a) 85 U–15 Zr, 4 hr at 1350°C. (b) 50 U–50 Zr, 4 hr at 1350°C.

DECLASSIFIED

some of these alloys or of pseudoalloys or of mixtures of zirconium, beryllium, and uranium with immiscible components such as ceramics or certain compounds. It is difficult to prepare zirconium-uranium alloys containing large percentages of uranium by melting, presumably because of segregation during freezing. Such alloys are readily made, however, by pressing and sintering the powders at much lower temperatures (Fig. 25).

Grain Growth. One of the outstanding accomplishments of powder metallurgy has been the development of thoriated tungsten wire. The addition of a small amount of thorium oxide to tungsten powder leads to the formation of a grain-boundary film which can inhibit grain growth. It is surprising that very little study has been made of the effect of similar additions to other metals in order to investigate the principles of this kind of grain-size control. For example, it would be interesting to see how various small additions affect the grain growth of the pure metals as shown in Figs. 4 and 5.

ACKNOWLEDGMENT

The writers gratefully acknowledge the help of many members of the Sylvania Metallurgical Laboratories in the preparation of this report. We especially thank N. P. Pinto, H. S. Kalish, R. P. Angler, H. W. Woods, J. F. Black, and Mrs. J. Brouthers.

C31

DECLASSIFIED

Some Long-range Aspects of Homogeneous Reactors

By J. A. Lane

Oak Ridge National Laboratory

Report ORNL-946 (Del.)

ABSTRACT

If homogeneous reactors can be made to work, they offer many worthwhile possibilities for the production of power and fissionable material. Consequently, a solution of the technical problems associated with homogeneous systems is extremely important for the long-range reactor program. The construction and operation of the proposed Homogeneous Reactor Experiment is the first major step in this direction, and the success of this experimental reactor will pave the way toward fuller utilization of the advantages of homogeneous or fluid systems.

The problem of reducing the cost of power from nuclear reactors is essentially one of reducing the capital cost of the reactor and its associated equipment. For this reason homogeneous reactors, by virtue of their fundamental simplicity and high possible power output, offer the best chance of achieving competitive industrial power.

The importance of initiating studies directed toward the development of a suitable thorium system should be emphasized, since a U^{233}-thorium thermal power breeder is potentially the most attractive possibility for economic power of the many systems considered.

INTRODUCTION

The following discussion is an attempt to assess the long-range future of certain types of homogeneous reactors on the basis of their utility as producers of power and fissionable material rather than from the standpoint of their technical feasibility. While such an economic viewpoint can be criticized as being unrealistic as long as fundamental problems associated with the operability of homogeneous systems remain unsolved, it does indicate the possible rewards of successful development work in this field. In view of the recent emphasis given to the experimental phases of the homogeneous-reactor program, it is hoped that a firm analysis of the scientific and technical aspects of this type of reactor can be presented in the not too distant future.

It has long been realized that homogeneous reactors are ideal from the standpoint of neutron economy, high heat removal, fuel handling, and simple internal structure and are therefore well suited to the purpose of power and fissionable material production. However, the practicability of such reactors, particularly those involving aqueous systems, necessarily depends on the solution of the many technical problems generally associated with homogeneous systems. Problems of chemical stability, nuclear control, and corrosion remain as barriers to the development of this type of reactor. The question of feasibility is particularly dependent on the nuclear behavior of the reactor in

DECLASSIFIED

the presence of gas bubbles. This can be demonstrated only through operation of an experimental prototype reactor.

In addition, the problems associated with the circulation of active fuel solutions require considerable study. The difficulty of maintenance of contaminated pumps and heat exchangers, for example, possibly enhanced by the corrosive nature of the fuel solution, emphasizes the importance of developing extremely reliable equipment for this purpose.

In spite of the advantages of homogeneous systems, little progress has been made in the design and construction of large-scale units because of the aforementioned technical difficulties. In addition to the bubble problem, which has been previously considered almost insuperable, the requirements of large amounts of heavy water moderator or enriched fuel necessary for criticality were believed to be difficult to achieve in the initial phases of the atomic energy program.

Studies at ORNL[1] now make it evident that the solution of the technical problems of stability, control, and maintenance of homogeneous reactors is worth a considerable effort because the successful development of this type of reactor offers the possibility of achieving many of the long-range objectives of the reactor-development program such as thermal breeding with the Th-U^{233} cycle, more economical plutonium production, and competitive industrial nuclear power. Also, the use of homogeneous reactors for mobile power is an attractive possibility.[2]

There are a number of recent developments which make prospects for achievement of success brighter than before. Some of these may be listed as follows:

(1) By increasing the pressure on the reactor, the bubble problem, previously considered almost insuperable, becomes theoretically manageable.

(2) The phase diagrams of the UO_2SO_4 and the UO_2F_2 systems in water[3,4] show adequate chemical stability of these systems up to temperatures sufficient for good power output (250 to 300°C).

(3) Corrosion rates of zirconium or 347 stainless steel by 250°C UO_2SO_4 solutions seem to be tolerable.[4]

(4) The recent decision to manufacture large quantities of heavy water will ultimately eliminate the bottleneck on this material.

(5) The possible expansion of isotope-separation facilities to process depleted wastes from reactors and increase the production of highly enriched material reduces the objection to the use of enriched fuels.

(6) A more recent estimate of the neutron losses in thermal breeders indicates an improved situation regarding the breeding gains. It now appears more likely than ever that a successful homogeneous thermal breeder, utilizing the Th-U^{233} cycle, is feasible. This would mean an increase in the potential supply of fissionable material as well as the possibility of power production at a cost comparable to existing steam-power plants.

The first major step toward the development of large-scale homogeneous reactors will be the operation of the Homogeneous Reactor Experiment[5] (HRE) at ORNL late in 1951. The importance of this experimental prototype reactor to demonstrate the nuclear and chemical stability of homogeneous systems and to study problems of operation and maintenance of associated equipment can not be overemphasized because a clearer insight into these questions is essential before large-scale units can be considered.

PROMISING TYPES OF HOMOGENEOUS REACTORS

By definition, homogeneous reactors include all types in which there is a homogeneous mixture of nuclear fuel and moderator and thus include a wide variety of mixtures of gases, liquids, and solids. Of the many possible combinations of fuel and moderator, however, only a few show promise of practical application. These are aqueous solution or slurry systems, which are best suited for the large-scale production of plutonium and power or for thermal breeders, and liquid-metal or molten-salt-solution reactors for small high-temperature mobile power units. The present emphasis of the homogeneous-reactor program is on these most promising types with only minor consideration being given to the many other possibilities.

The advantages of homogeneous systems are in general those attributable to the fluid nature of the fuel and to a lesser degree to the fluid moderator. For this reason heterogeneous arrangements of liquid fuel and solid or liquid moderator, which possess most of the advantages of homogeneous systems, may be equally applicable for many of the stated uses of homogeneous reactors. It may be that the proper path of development of large-scale reactors should be defined more by the physical nature of the nuclear system rather than by the distribution of fuel and moderator.

ADVANTAGES OF AQUEOUS HOMOGENEOUS REACTORS

High Specific Power

Homogeneous reactors may be operated at specific power levels of 200 megawatts per ton of uranium, whereas natural-uranium heterogeneous reactors operate in the range of 2 to 5 megawatts per ton. The high specific power is particularly important if the total amount of uranium available is limited. Also this low fuel inventory combined with high burn-up permits the economic production of power from an initial fuel charge, impractical with heterogeneous type reactors.

c 33

DECLASSIFIED

High Power Output

In a heterogeneous system, the temperature rise within the fuel elements limits the maximum heat flux and consequently the total power output of the reactor. In a homogeneous reactor, because of intimate contact of fissionable material and coolant, the heat transfer inside the reactor does not limit the possible power output. Assuming that the gas generation can be handled adequately, the only limitation on ultimate power output is the maximum fuel circulation rate which can be achieved. This means that a single homogeneous reactor can produce considerably more power and plutonium than a practical size heterogeneous reactor; this should result in lower fixed costs and lower operating costs per unit of power output or gram of plutonium produced.

High Possible Burn-up

In a heterogeneous reactor radiation damage resulting in distortion of solid-fuel elements limits the irradiation time of a given fuel charge. Although this is relatively unimportant for the production of plutonium with a minimum isotopic concentration of Pu^{240}, high burn-up is essential if it is desired to produce economical power without plutonium production. In addition to radiation damage the build-up of fission-product poisons gradually reduces the reactivity of a heterogeneous system. In a homogeneous reactor essentially complete burn-up of the fuel in a given charge is possible since the fuel suffers no permanent radiation damage and the fission-product poisons may be continually removed.

Radiation damage to the solid moderator in a heterogeneous reactor may limit the useful lifetime of the reactor, whereas the moderator decomposition in the homogeneous system is handled on a continuous basis. If corrosion problems can be met, homogeneous reactors should have a considerably longer life than the heterogeneous type.

High Neutron Economy

Homogeneous reactors have the highest neutron economy, since there are no structural materials or coolants in the core and the fission-product poisons may be continually removed. This feature, combined with high specific power, makes thermal breeding most attractive in homogeneous systems.

Simple Fuel-reprocessing Systems

Homogeneous systems require no metallurgical processing and possibly less chemical processing by virtue of lower decontamination requirements. The holdup in the chemical plant is lowered and the required cooling period is decreased for homogeneous fuel solutions. Off-gas problems during dissolving are eliminated. The possibility exists of continuous decontamination and recovery of plutonium with a negligible Pu^{240} concentration.

Less Complicated Control System

Referring to Fig. 4, it is seen that the critical size of aqueous homogeneous reactors varies with concentration, i.e., D_2O/U ratio. Thus, unlike heterogeneous reactors, it is possible to control a homogeneous reactor by varying the concentration of the fuel solution. Moreover, if the size of the reactor core is fixed, the reactor will operate at an equilibrium temperature, corresponding to a given fuel concentration. At temperatures above this equilibrium value the density of the moderator will be too low to support the nuclear chain reaction. This highly sensitive negative temperature coefficient of reactivity thus serves to keep the pile stable at a given temperature independent of power output. Since the power output is proportional to the temperature rise of the fuel solution within the reactor, control of the power may be achieved by varying the temperature of the fuel solution leaving the external heat exchanger, which in turn depends on the demands from the turbogenerator unit. This method of control is achieved without the use of mechanical shim or regulating rods, which are objectionable from the standpoint of neutron economy.

Inherent Safety

It has been pointed out that the greatest potential hazard of thermal reactors depends on the amount of long-lived fission products present in the reactor at any time. In a homogeneous reactor there is the possibility that these may be continually removed to eliminate the danger.

Utilization of Recombination Energy

The recombination of the hydrogen and oxygen formed in the dissociation of moderator provides heat in convenient form for superheating steam and increasing plant efficiencies.

Simple Internal Structure

Since the core of a homogeneous reactor consists merely of a pressure shell, the design of this type of reactor is fundamentally less complicated than that of a heterogeneous reactor with its complex cooling system and moderator structure.

Easier Fuel Handling

The fuel solutions may be charged or discharged on a continuous basis without the difficult handling problems of solid-fuel reactors.

DECLASSIFIED

DISADVANTAGES OF AQUEOUS HOMOGENEOUS REACTORS

High Cost of Moderator

Because of its nuclear properties the use of an H_2O moderator, highly desirable from the standpoint of economy and chemical reprocessing of fuel solutions, is only possible in systems using enriched uranium containing about 3 per cent or greater concentration of U^{235}. The critical size of such reactors, moreover, is too small to permit the extraction of large quantities of heat, since pipe sizes and heat exchangers must be kept subcritical. In natural-uranium or slightly enriched-uranium homogeneous systems large amounts of D_2O or possible mixtures of H_2O and D_2O are required. The availability of D_2O may well be one of the most important limitations to the development of large-scale natural-uranium or slightly enriched-uranium homogeneous systems.

Induced Activity of Pumps and Heat Exchangers

The delayed neutrons in the fuel solutions circulated through pumps and heat exchangers cause induced activity and increase problems of maintenance of equipment.

Corrosive Nature of Pile Solutions

Owing to the corrosive nature of the fuel solutions the expected lifetime of equipment in the fuel-recirculation system will be less than that with conventional coolants. Slurries will be more advantageous from this standpoint than aqueous solutions.

High Cost of Pressure Shell

To be efficient power producers, homogeneous reactors must operate under moderately high pressures and temperatures. A large pressure shell to meet these requirements is difficult to design and fabricate and is somewhat beyond ordinary engineering practice. For this reason the size, and thus the operating conditions of a large-scale homogeneous reactor, may be selected on the basis of what is a feasible pressure shell rather than from purely economical considerations.

Gas Problems from Decomposition of Moderator

It is not yet clear whether the formation of bubbles in a homogeneous reactor presents a severe control problem or actually contributes to the stability of the reactor. This unknown more than any other has hindered the development of this type of reactor. Under certain conditions the gases form explosive mixtures which are considered to be a potential hazard. It is expected that experiments in the prototype reactor will throw light on the complex bubble problem.

PREVIOUS INVESTIGATIONS OF AQUEOUS SYSTEMS

Aqueous-solution reactors for the production of plutonium were suggested in the early phases of the Manhattan Project but were rejected in favor of the heterogeneous type because the requirements of enriched fuel or large amounts of heavy water would delay the plutonium-production program.

Proposals for slurry reactors, fueled with natural uranium and moderated with heavy water, were initially investigated at Columbia University under the direction of H. C. Urey and C. F. Hiskey.[6] Late in 1943 most of the group working on this problem was transferred to the Metallurgical Laboratory in Chicago where the work was continued for about a year, at which time the press of problems connected with Hanford interfered.[7]

Most of the early work on slurries was directed toward finding a suitable slurry and proper materials of fabrication, with major emphasis on uranium oxide systems. Extensive plans were made to measure the relative amounts of abrasion and erosion by the slurries on heat exchangers, pumps, and valves, but no large-scale experiments were actually completed.

However, a number of static and dynamic corrosion and abrasion tests were made on a laboratory scale. In addition, work was started on fundamental studies of the variation in particle size and chemical composition of different slurries with time.

In 1945 work was started at Oak Ridge National Laboratory on the design of a low-temperature low-pressure homogeneous-solution pile operating at 30,000 kw to serve as an experimental tool and a breeder pilot plant. Enriched uranyl sulfate and uranyl carbonate solutions were considered as fuels. Several designs were studied[8] but the project was discontinued when no clear solution was found to the problem of reactor stability in the presence of gas bubbles formed by radiation-induced decomposition of the moderator. Operation at low temperatures and low pressures, while simplifying engineering problems of design and corrosion, magnifies the difficulty of nuclear control.

Two low-power water boilers have been built and operated successfully at Los Alamos.[9] The one of significant power output has been operated at 30 kw with a 12-in.-diameter core, containing an ordinary water solution of uranyl nitrate enriched to 89 per cent U^{235} and reflected by beryllium oxide. At this power level little or no difficulty with gas formation is experienced other than the explosive hazard of the large volume of $H_2 + O_2$. A reactor of this type has been approved for construction at North Carolina State College which will be the first to be operated by private enterprise.

The most recent attempt to attack the problems as-

714 035

DECLASSIFIED

sociated with homogeneous systems is represented by the Homogeneous Reactor Experiment, recently approved for construction at the Oak Ridge National Laboratory. Construction of the building is now under way and operation of the reactor is scheduled for August 1951. The fuel will be highly enriched U^{235} as uranyl sulfate dissolved in light water contained in an 18-in.-diameter core. This core is surrounded by a heavy water reflector. The reactor will operate at 250°C and 1000 psi pressure and produce up to 1000 kw of heat. These operating conditions, it is believed, will substantially eliminate the bubble problem since the high temperature serves to accelerate the recombination of hydrogen and oxygen in the core and the high pressure reduces the volume of bubbles to a tolerable point.

Although the Homogeneous Reactor Experiment is designed for the initial investigation of the uranyl sulfate solution reactor, the equipment is flexible enough to permit the study of other promising systems. This is important because so much depends on the results of future development work that the selection of the most promising homogeneous system from the long-range standpoint is impossible at the present time.

GENERAL DESIGN CONSIDERATIONS

There are a large number of promising combinations of the variables which must be thoroughly investigated before establishing a valid direction for a large-scale homogeneous-reactor program. These are discussed briefly in the following paragraphs.

Choice of Fuel

From the standpoint of neutron economy and the production of fissionable material, the thorium-U^{233} system is more advantageous than the U^{235}-U^{238}-plutonium system. In addition, the use of thorium increases the potential supply of nuclear fuel. Unfortunately no suitable thorium solution is known at the present time except the nitrate with the N^{15} isotope, and the use of thorium may be limited to slurry-type reactors.

Choice of Moderator

While D_2O-moderated reactors have the advantage of higher neutron economy and greater latitude with respect to size and degree of enrichment, the use of H_2O provides a cheap moderator and possible reduction in the size of the reactor. The chemical reprocessing of depleted wastes from H_2O-moderated systems is simplified. Light water reactors may have application as mobile power units but are less attractive for the production of fissionable material owing to their low neutron economy.

Choice of Solution

The phase diagrams of aqueous solutions of uranyl sulfate and uranyl fluoride shown in Figs. 1 and 2 indicate that the chemical stability of these systems is satisfactory up to 250°C. The sulfate system is less corrosive than the fluoride system but has the disadvantage of lower neutron economy due to the parasitic absorption of thermal neutrons by the sulfur. The nitrate system using the N^{15} isotope for satisfactory neutron economy may be applicable for operating temperatures up to 180°C.

The use of a slurry of an insoluble uranium or thorium compound offers the advantage of higher neutron economy and no corrosion problems and may ultimately be more attractive than a fuel solution. The major problems introduced by this system involve the preparation of a stable slurry and the development of pumps suitable for slurries. Attempts to prepare stable slurries are thus far encouraging,[10] and work in this direction is continuing on an expanding scale. Studies of the fundamental behavior of solid-liquid systems are being initiated.

Degree of Enrichment

There is a whole spectrum of homogeneous reactors depending on the equilibrium concentration of fissionable material at which the reactor runs. At one end there is the highly enriched reactor for producing power; at the other end, the low-enriched plutonium producer or thermal breeder. In between there are slightly enriched-U^{235} systems which make use of material from the intermediate stages of an isotope-separation plant such as K-25. If, for a particular application, the size of the reactor must be held within certain limitations, the required enrichment depends on the permissible concentration of the fuel solution. If the size of the reactor is not fixed, the degree of enrichment depends on a balance of the lower cost and engineering advantages of the smaller highly enriched machines against the cost and use of enriched fuel. Since in all cases of reactors producing plutonium for military use the depleted wastes must be returned to an isotope-separation plant for reprocessing, no particular prejudice in favor of natural-uranium reactors exists and the question of proper enrichment becomes a purely economic one.

Reactor Configuration

The simplest configuration consists of a spherical reactor core which may or may not be surrounded by a reflector or blanket. Attempts to design the reactor core so that the reactivity is essentially independent of density changes and thus eliminate the bubble problem usually result in large core volumes and shapes difficult to fabricate. Certain features of the design of

DECLASSIFIED

the reactor core are influenced by the method of removing heat and gas bubbles as discussed in the following section.

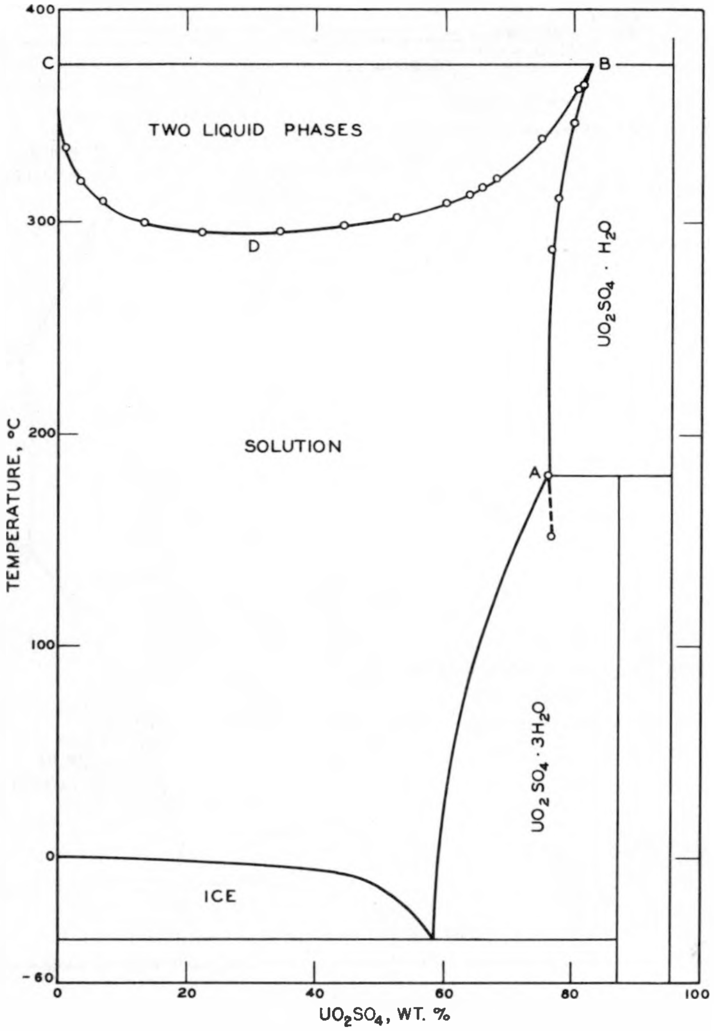


Fig. 1 — Phase diagram for system uranyl sulfate – water.

Method of Heat Removal

In the most conventional system the heat is removed by pumping liquid through the reactor core and heat exchangers as proposed in the HRE. By introducing the liquid through inlets tangential to the reactor core, a circular motion of the liquid is produced which drives bubbles toward a vortex in the center and reduces the volume of gas present at any time. Figure 3 shows a photograph of circulating liquid and gas bubbles in a plastic sphere.

In the so-called "boiling reactor," heat is removed by vaporization of the liquid in the core. The vapor is subsequently condensed in the external system and returned to the core by gravity or pumps. In this manner the holdup of active fuel in the external system is reduced or eliminated, the activity of pumps and heat exchangers decreased, and the pumping power reduced. Since the condensate is less corrosive, problems of equipment maintenance are considerably reduced. The main objections to this system are the questionable feasibility of control in the presence of large amounts of bubbles and the difficulty of providing adequate surface for the release of the large volume of vapor generated. The decrease in the density

C 37

of the moderator due to the presence of the vapor substantially increases the critical size of the reactor.

A modification of the boiling reactor involves removal of the heat by flash vaporization of the fuel solution external to the reactor core. The heat exchangers in a conventional system are replaced with flash vaporizers which may be smaller, less complex, and more reliable. Since a large pressure drop is required to release the necessary amount of heat, the power consumed by pumps is increased by at least a factor of 3 over the conventional system.

On the basis of our present knowledge of aqueous homogeneous systems three specific types of reactors look promising from the long-range standpoint. These are: a large D_2O-moderated uranyl sulfate reactor for producing plutonium and power; a similar reactor, possibly of different size, for a stationary mobile power unit; and a slurry type homogeneous thermal breeder using thorium and U^{233}. These reactors are described in the following sections.

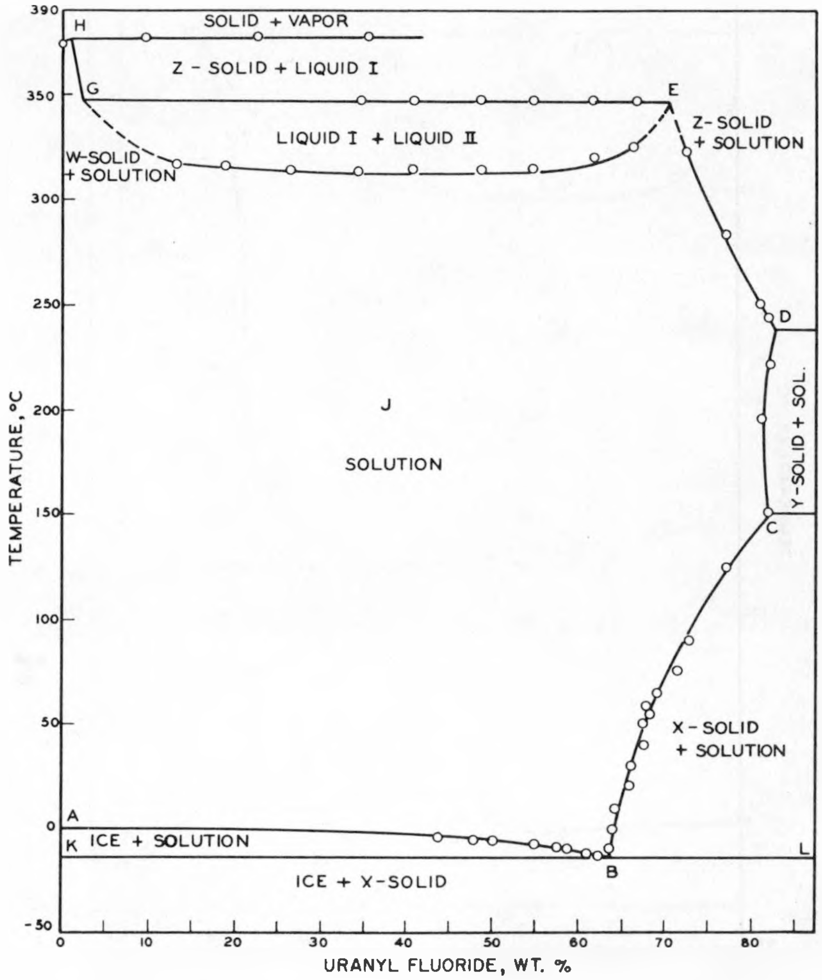


Fig. 2 — Phase diagram for the system uranyl fluoride–water.

THE PLUTONIUM-PRODUCER POWER REACTOR

Although the ultimate design of the most suitable large-scale homogeneous reactor for the simultaneous production of plutonium and power may well involve other chemical systems and reactor configurations, the use of a solution of uranyl sulfate in D_2O appears to be feasible. Both chemical stability and radiation stability of uranyl sulfate up to temperatures sufficient for good power output (250°C) seem assured, and zirconium, titanium, or 347 stainless steel can be used as the material of construction.

DECLASSIFIED

The plutonium-producer—power reactor described in Report ORNL-855 operates at 10^6 kw and uses an 0.8 per cent U^{235} fuel as a solution of uranyl sulfate in D_2O. This affords an excellent compromise between the conflicting demands of fuel cost and size of reactor. In the proposed design the reactor core consists of a 24-ft-diameter spherical shell, 5¼ in. thick, with a 347 stainless steel liner. The fuel solution is introduced through tangential inlets in the shell at the rate of 100,000 gal/min. The circular motion of the liquid in the core drives the gas bubbles toward a vortex in the center and reduces gas holdup. The reactor operates at an equilibrium temperature of 250°C and 1000 psi pressure. The fuel solution leaves the core through exit pipes located at the top and bottom of the reactor and circulates through tubes of a number of evaporator type heat exchangers. These produce steam at 194°C and 200 psi pressure which is superheated by heat from the $D_2 + O_2$ recombination reaction. The steam operates a conventional low-pressure extraction turbine with an electrical generator unit. The net power output will amount to about 230,000 kw. Since the available heat from the recombiner is limited, an auxiliary oil- or gas-fired superheater may be desirable to reduce the amount of water vapor in the turbine exhaust.

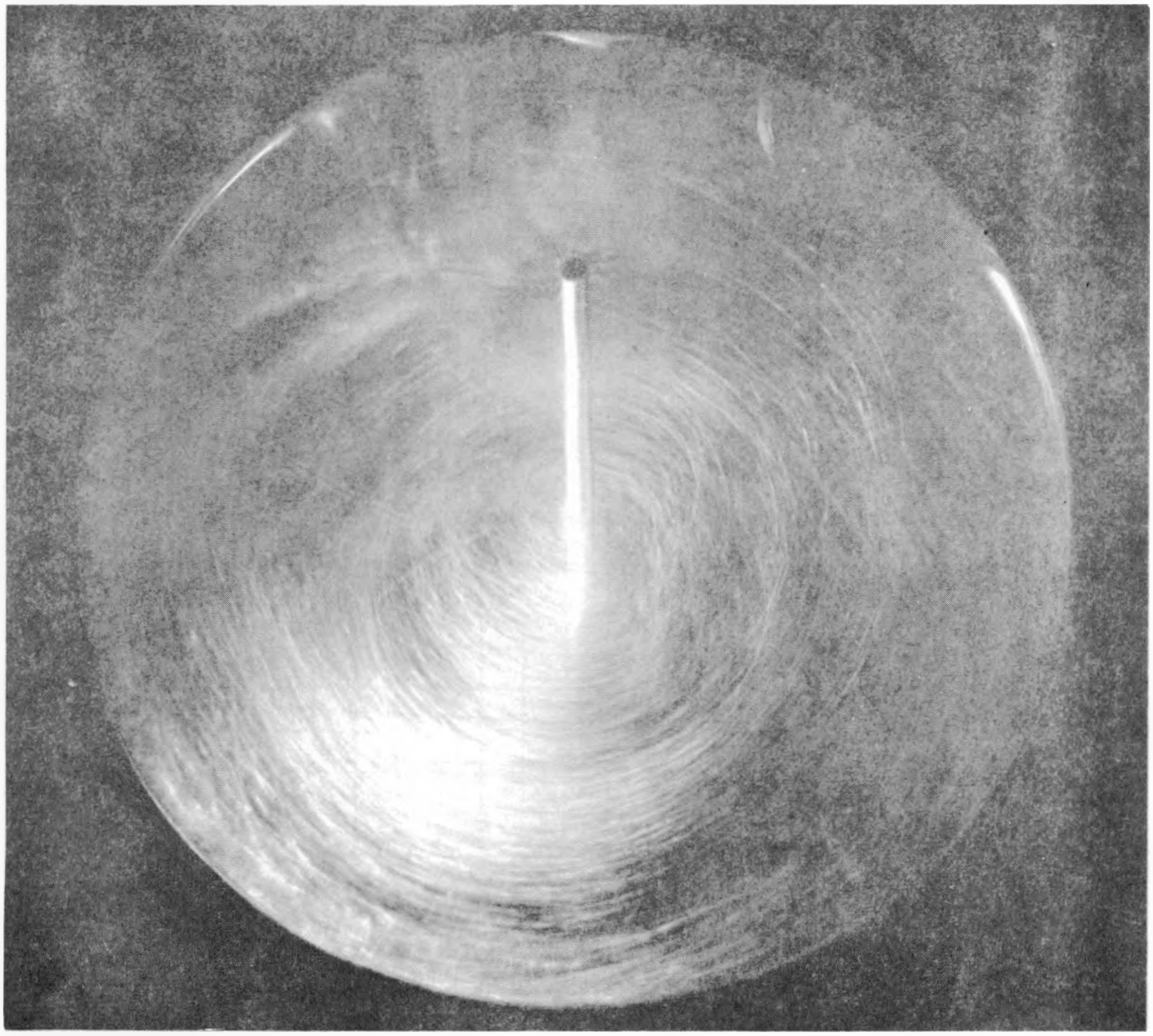


Fig. 3—Bubble tracks.

One of the most interesting features of the reactor is the possibility of a greatly simplified control sys-

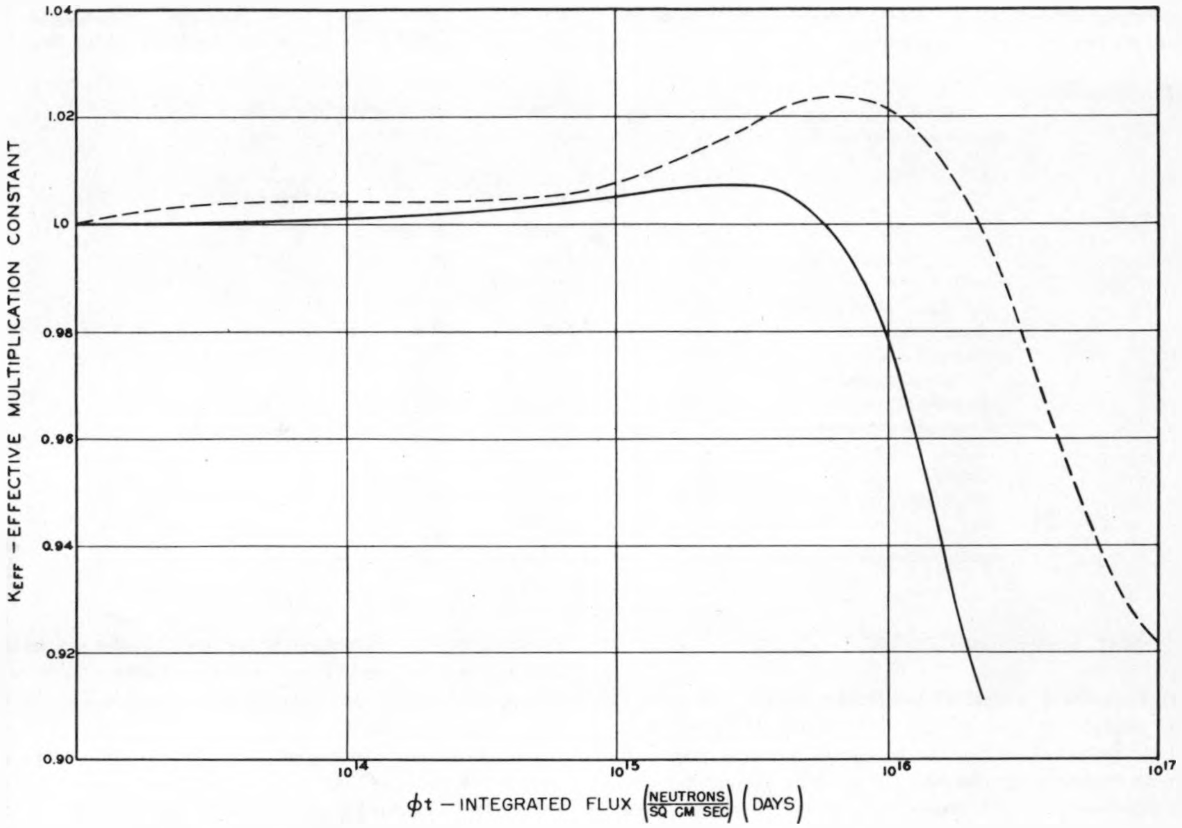


Fig. 6—Time variation of multiplication constant for homogeneous UO_2SO_4-D_2O solutions at 250°C. ---, 0.8 per cent U^{235}, 22-ft spherical core. ——, 1.54 per cent U^{235}, 9-ft spherical core.

tem. Instead of mechanical shim rods, over-all changes in reactivity are compensated for by varying the concentration of uranium in solution. Also the regulating controls for minor fluctuations in reactivity may be unnecessary since the sensitive negative temperature coefficient of reactivity makes the reactor self-stabilizing at any given operating temperature, dependent on the uranium concentration. An increase in reactivity which tends to produce higher temperatures is offset by the increased volume of gas and the decrease in density of the moderator. The power output of the reactor may therefore be controlled by the temperature of the fluid returning from the heat exchangers. This means the power output in the core will respond to the heat removed in the heat exchangers or to the demands of the turbogenerator unit. Emergency shutdowns are effected by discharging a part of the fuel solution in the core to dump tanks.

THE AQUEOUS POWER UNIT

If the solubility of plutonium sulfate in D_2O is sufficient under the desired operating conditions, it may be possible to operate the reactor described in the previous section for power alone by allowing the plutonium to accumulate and burn along with the U^{235}. In such a system continual removal of the gaseous and solid fission products would be necessary to prevent the long-term build-up of poisons. Two alternate methods of fueling are possible. Either the entire fuel charge can be replaced at regular intervals determined by the variation of reactivity with time as shown in Fig. 6 for two enrichments and reactor sizes, or small amounts of U^{235} can be added continually to make up for the conversion loss.

heat exhangers by suitable pumps. The system is somewhat analagous to a conventional steam-power plant, with the heat exchangers for the core solution replacing the boilers and the heat exhangers for the blanket corresponding to the feed-water heaters.

Table 4—Comparison of Current Estimated Neutron Losses with Old Estimate

	Losses, %			
	New estimates			Old estimates
Cause	g = 500 cc/g	g = 1000 cc/g	g = 1500 cc/g	g = 100 cc/g
Foreign atoms in core	4.0	8.0	13.0	1.5
Tank absorption	1.0	0.9	0.9	1.0
Delayed neutrons	0.5	0.5	0.5	2.0
Poison absorption	1.7	1.7	1.7	
Isotope absorption	0.6	0.6	0.6	1.5
Chemical processing	0.3	0.3	0.3	3.5
D_2O in blanket	0.3	0.3	0.3	1.0
Escape	1.0	1.0	1.0	1.5
Absorption by Pa	0.8	0.8	0.8	1.5
Total	10.1	14.1	19.1	13.5

THERMAL POWER BREEDER

An important aspect of the future success of industrial nuclear power is the possibility of converting fertile material to fissile material by breeding and thereby increasing the total available supply of fissionable material. A homogeneous U^{233}-thorium unit offers an excellent means of realizing this, since recent estimates indicate that breeding gains of the order of 0.2 are possible. In addition, significant amounts of power can be produced as a by-product. The electrical output of such a system would be about 1,250,000 kw. An important advantage of the breeder is that it is a combination producer of power and fissionable material which is independent of an isotope enrichment plant, since the separation and recovery process is chemical in nature. It may well be that the U^{233}-thorium breeding system, by avoiding the costly enrichment cycle via diffusion-plant operation, will be more attractive than the plutonium and power system based on slightly enriched or normal uranium.

The thermal breeder considered in Report ORNL-855 is a 500,000 kw aqueous power reactor similar to the HRE unit but with necessary modifications to handle the considerable increase in power. The reactor consists of an enriched core containing a solution of U^{233} in D_2O, presumably as uranyl sulfate, surrounded by a D_2O slurry of thorium oxide. The D_2O slurry can be replaced by Li for tritium production. Both the core and the blanket material are circulated through Steam from the core heat exchangers drives a standard turbogenerator unit. The usual condensers, feed-water pump, and other auxiliaries are required as in any steam-power station.

From the breeding viewpoint, the success of such a reactor hinges largely on the neutron losses. Using the above system as a basis, with the reactor core at 250°C and the blanket at 200°C, the neutron losses have been computed for three values of g (the ratio of D_2O to U^{233}) and the estimates compared with those previously given by Wigner, Weinberg, and Young.[11] This comparison is shown in Table 4.

The important aspect of the data shown in Table 4 is that the neutron losses may be held to about 14 per cent with one-tenth the U^{233} concentration previously considered. With the lower concentration the inventory of uranium in the reactor is reduced, materially decreasing the doubling time. In addition, there are several other developments which make thermal breeding look attractive. These are summarized as follows:

(2) Chemical processes such as Redox which involve losses per cycle of less than 0.1 per cent have been routinely demonstrated. At the time of the Wigner report there was grave doubt about the feasibility of a chemical cycle with less than 1 per cent loss.

(3) The capture of D_2O (σ_a = 0.0008b) is less and the available purity (99.84 per cent) is greater than Wigner assumed. This makes a breeder at only 1 or 2 g

U/liter, instead of 10 g U/liter, a possibility, and thus drastically reduces the doubling time.

(4) Delayed neutrons from 23 are only 0.24 per cent instead of 0.8 per cent as given by Wigner. This complicates control but improves breeding.

(5) Zirconium has appeared on the scene as a feasible tank material of low-absorption cross section and good mechanical properties.

(6) Aqueous uranyl sulfate appears to be a feasible reactor fluid.

It is thus evident that the outlook for thermal breeding is much better now than it was in 1945.

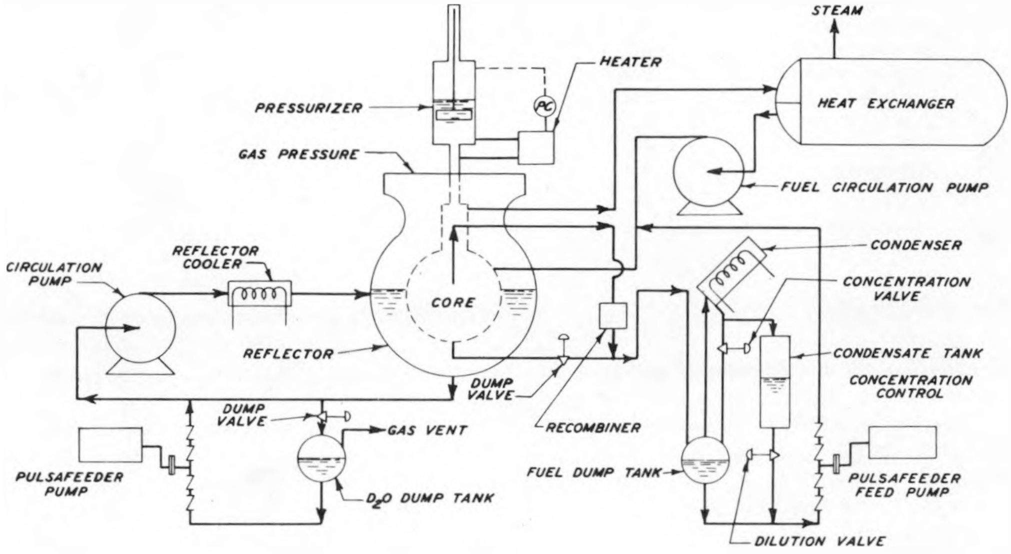


Fig. 7—Homogeneous-reactor experiment, simplified flow diagram.

THE ROLE OF THE HRE IN HOMOGENEOUS-REACTOR DEVELOPMENT

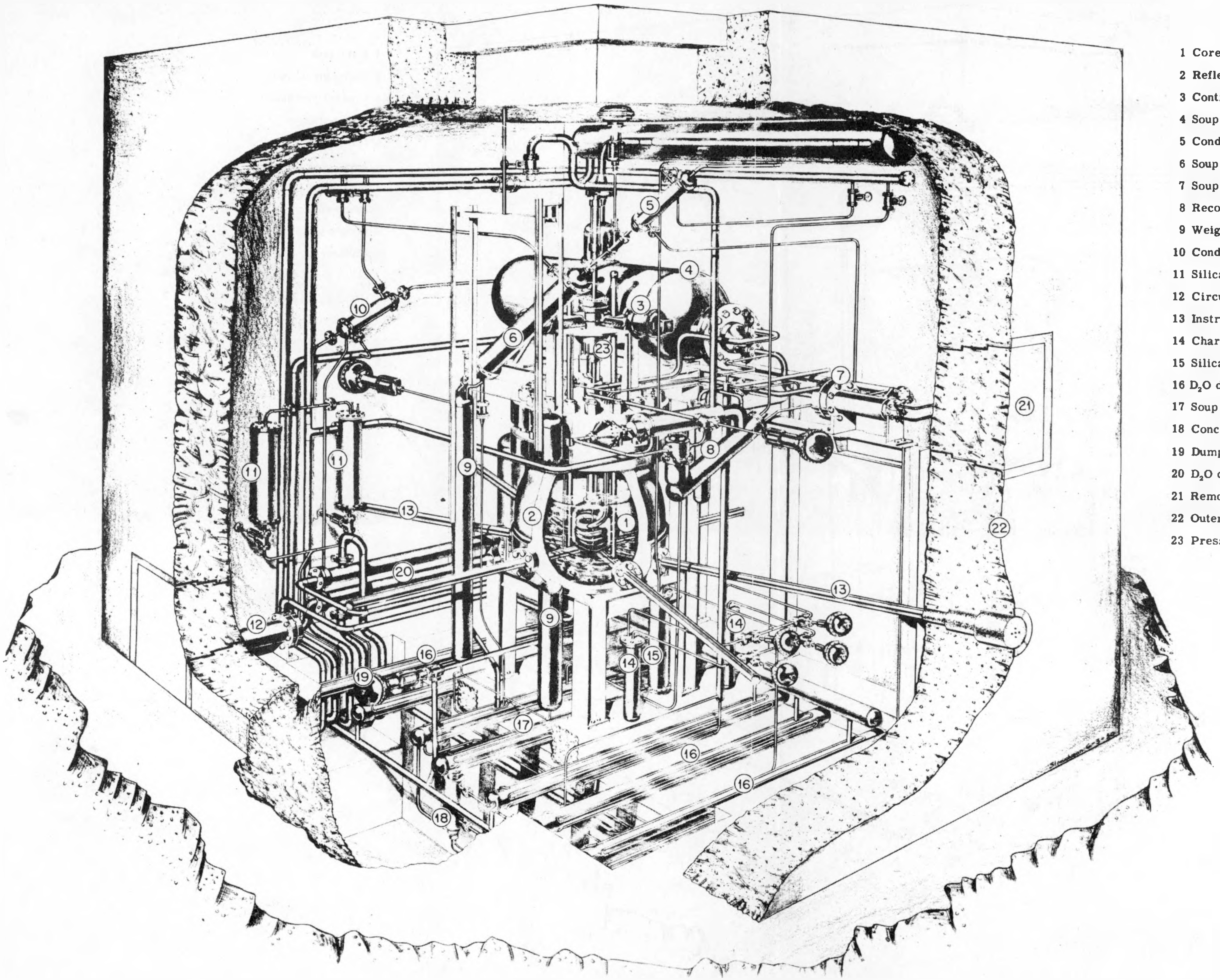
The previous sections of this paper have indicated that successful aqueous homogeneous reactors may be capable of producing power and fissionable material very much more economically than any heterogeneous systems which have been proposed thus far. It is therefore probable that aqueous homogeneous reactors may be the main line of development for large-scale stationary power and Pu- or U^{233}-producing reactors. In addition, nonaqueous homogeneous reactors may be very attractive for highest performance mobile power systems.

Although the long-range future of aqueous homogeneous reactors looks promising, the inherent difficulties of homogeneous systems must be overcome before embarking on a full-scale enterprise. Crucial problems of corrosion, chemical stability, and control must be thoroughly understood before the actual designing of large-scale reactors. Since many of the problems can be answered only by actual operation of a homogeneous reactor, it seems evident that the proper path of development involves the construction of a sequence of small and cheap experimental prototype reactors. The successful operation of these reactors will demonstrate the feasibility of homogeneous systems and provide the most direct and coherent solutions to the many design problems.

The Homogeneous Reactor Experiment described in Reports ORNL-730 and ORNL-731 is conceived as the first in this sequence of experimental reactors. Figure 7 shows a flow diagram of the proposed operation and Fig. 8 is a layout of important components. Essentially, the reactor consists of an 18-in.-diameter core containing a solution of 30 g per liter of highly enriched uranium as UO_2SO_4 in H_2O. The core is surrounded by a D_2O reflector contained in a steel pressure shell. The reactor operates at 250°C and 1000 psi pressure and produces a maximum of 1000 kw of heat. This is removed by pumping the fuel solution through an evaporator type heat exchanger. Steam produced in the evaporator will drive a turbogenerator unit producing about 150 kw of electrical power.

The most significant aspect of the HRE is the possibility of closely duplicating the actual operating conditions of large-scale reactors. This is true not only

DECLASSIFIED



1 Core tank
2 Reflector vessel
3 Control-rod drive
4 Soup boiler
5 Condenser
6 Soup condenser
7 Soup pump
8 Recombiner
9 Weight tanks
10 Condenser
11 Silica gel absorbers
12 Circulating pump
13 Instrument tubes
14 Charcoal adsorbers
15 Silica gel absorber
16 D_2O dump tanks
17 Soup tanks
18 Concentration heater
19 Dump valve
20 D_2O cooler
21 Removable plug
22 Outer shield
23 Pressurizer

Fig. 8—Homogeneous-reactor experiment. General arrangement of equipment.

714 043

DECLASSIFIED

with respect to temperature and pressure but also for the fission density in the fuel solution as shown in Table 6. The reduction in size is made possible by substituting a light water highly enriched-uranium system for the heavy water moderator and slightly enriched fuel. Thus, conditions of bubble formation and control stability can be reproduced on a small scale.

Table 6 — Comparison of Power Densities of Proposed Homogeneous Reactors

	U^{233} power breeder	Plutonium producer	HRE
Grams U/liter	1	90	30
Power density, kw/liter	100	5	5 – 20
Total power, megawatt	500	1000	0.25 – 1

Actually the HRE is almost a scale model of a U^{233} power breeder rather than the aqueous plutonium-producer reactor, and for this reason extrapolation from the HRE to the very large-scale reactors will not be completely reliable. It may well be that the design and construction of a moderately sized reactor operating at about 50,000 kw will be necessary before considering the construction of large-scale machines.

The emphasis of the proposed experimental program for the HRE will be on questions of over-all operational feasibility of homogeneous reactors which are not susceptible to component research. These are summarized below, roughly in the order of relative importance.

(1) Kinetics of gas production in the reactor core and the effect of bubbles on control stability.

(2) Methods of suitable reactor control and reliability and maintenance of reactor material and equipment.

(3) Chemical and radiation stability of the fuel solution.

(4) Methods of gas removal, recombination of H_2 + O_2, and disposal of fission-product gases.

(5) Operability and maintenance of the power-generation system.

In general, the successful operation of a circulating-fuel fairly high-power nuclear reactor will provide a wealth of over-all experience and information which can never come from component experimentation and which will establish with some assurance the proper direction for the development of large-scale reactors.

NONAQUEOUS SYSTEMS

Although the aqueous systems described previously are generally applicable to many of the long-range objectives of the reactor program, such systems are limited by the temperatures which can be achieved because of the increasing difficulties of corrosion and chemical stability at the higher temperatures. Since the efficiency of the power-generating system increases with the temperature of the fuel solution, nonaqueous nuclear-fuel systems operating at relatively high temperatures offer the possibility of improved power cycles.

Not all the promising types of high-temperature nonaqueous reactors involve the homogeneous arrangements of fuel and moderator to which this discussion is limited. Many heterogeneous arrangements of liquid fuel and/or liquid moderator have considerable merit and may be more applicable for some uses than purely homogeneous systems. Consequently, it is realized that a consideration of homogeneous reactors alone does not present a complete picture of possible future types of nuclear reactors. However, a true assessment of the over-all program depends strongly on decisions and development work now in progress and therefore must be deferred.

In the following paragraphs, proposals involving nonaqueous types of homogeneous reactors are reviewed briefly.

Gaseous Systems

Pure gaseous reactors using UF_6 as a fuel, as suggested by Hull,[13] are not practical because of the large critical size. However, mixed solid and gas systems using a beryllium moderator are reasonable in size and have the advantage of gaseous systems, i.e., no radiation damage, simple chemical reprocessing, and certain safety features. Disadvantages are the corrosive nature and low heat capacity of the UF_6.

Solid-core Homogeneous Reactors

Numerous suggestions for solid-core reactors in which both the fuel and moderator are solid have appeared in the literature. One of the first of these consisted of a homogeneous mixture of graphite and uranium oxide pellets cooled by helium or bismuth-lead alloy. The original Daniels' pebble pile was similar in nature, using a mixture of BeO plus uranium oxide cooled by helium.[14] Recently Daniels has proposed a high-temperature experimental power reactor made of graphite bars impregnated with uranium oxide and cooled by nitrogen or helium.[15] Thermal and intermediate reactors consisting of uranium or plutonium-beryllium alloy cores, cooled by helium or liquid metal, have been studied.[16] At least one suggestion proposes the use of fluidized beds similar to those involved in catalytic cracking units common to modern oil refineries.[17]

A low-power research reactor consisting of a homogeneous arrangement of graphite blocks impregnated

714 044

DECLASSIFIED

with enriched-uranium oxide and cooled with heavy water has been proposed by Thompson and Fahrner of North American Aviation, Inc.[19] This reactor has the advantage of low cost and high inherent safety. At the proposed operating level fuel depletion and poisoning rates are low enough to permit operation for 10 years without fuel replacement so the fuel-handling difficulties usually associated with solid systems are not particularly objectionable.

Solid-core type homogeneous reactors do not generally possess the advantages of fluid and fluidized reactors. The fuel and moderator are easily removed only if they are in pebble or powder form. Solid fission products are retained in the core. Enriched fuel is usually required. However, such reactors are particularly well suited to high-temperature operation and do not require a particular pattern of fuel material. The active material is kept in the core, facilitating the maintenance of external equipment.

ACKNOWLEDGMENT

This manuscript is an outgrowth of Report ORNL-855, A Preliminary Study of the Feasibility of Large Scale Homogeneous Reactors, to which many members of the Oak Ridge National Laboratory contributed. In particular, the author wishes to acknowledge the assistance of members of the Long Range Planning Group, R. B. Briggs, N. F. Lansing, L. C. Noderer, and J. M. Stein, as well as the encouragement and advice of the Research Director, A. M. Weinberg.

REFERENCES

1. A Preliminary Study of the Feasibility of Large Scale Homogeneous Reactors, Report ORNL-855, Oak Ridge National Laboratory Long Range Planning Group, Aug. 16, 1950.
2. Report of the Technical Advisory Board to the Technical Committee of the Aircraft Nuclear Propulsion Program, Report ANP-52, Aug. 4, 1950.
3. C. H. Secoy, The System Uranyl Sulfate-Water. II. Temperature Concentration Relationship above 250°C, Report ORNL-98, July 7, 1948.
4. C. E. Winters and A. M. Weinberg, Homogeneous Reactor Experiment Feasibility Report, Report ORNL-730, July 6, 1950.
5. C. E. Winters, Report to the Reactor Safeguard Committee, Report ORNL-731, June 7, 1950.
6. H. C. Urey, Heavy Water-Slurry Pile, Report A-743, June 30, 1943; H. D. Smyth, E. P. Wigner, and H. C. Vernon, Memorandum from P-9 Committee, Revised November 3, 1943, Report CS-853.
7. L. A. Ohlinger, Resumé of Engineering Design for a P-9 Homogeneous Slurry Pile, Report CE-3477, Nov. 26, 1943; J. H. Chapin and F. R. Ward, Terminal Report of Engineering Investigations of P-9 Homogeneous Pile, Report CE-1149, Jan. 13, 1944.
8. L. W. Nordheim, Physics Division Report for Month Ending November 30, 1945, Report MonP-33; H. C. Ott, The Homogeneous Natural Uranium-D_2O Pile as a Source of Power, Report MonC-374; F. Armistead and K. Way, Summary of New Pile Report Studies, Report M-3194, Clinton Laboratories, 1946.
9. C. P. Baker et al., Water Boiler, Report LA-134, Aug. 4, 1944; F. L. Bentzen, D. P. King, et al., High Power Water Boiler, Report LA-394, Sept. 19, 1945.
10. C. E. Winters, Homogeneous Reactor Experiment: Quarterly Progress Report for Period Ending August 31, 1950, Report ORNL-826.
11. E. P. Wigner, A. M. Weinberg, and Gale Young, Preliminary Calculations of a Breeder with Circulating Uranium, Report MUC-EPW-134, Dec. 19, 1944.
12. A. J. Cruikshank and D. J. Littler, A Determination of η (Thermal) of Uranium 233, Report CRP-378, April 1948.
13. D. E. Hull, Possible Applications of UF_6 in Piles, Report MonN-336, July 1, 1947.
14. F. Daniels, High Temperature Pebble Pile: Minutes of Lecture April 14, 1945, Report CF-2860 (5); J. E. Willard and F. Daniels, Current Status of Work on High Temperature Oxide Pile, Report MUC-JEW-127, June 21, 1946.
15. F. Daniels, Suggestion for an Experimental Power Reactor, Report ANL-4448, April 1950.
16. Gale Young, Sketch of a Gas Turbine Power Plant, Report CF-3290, Aug. 10, 1945; A. J. Dempster, Physics Division Report for Month Ending April 15, 1945, Report CF-2926; Gale Young, Regard Normal Piles for Power, Report MUC-GY-39, Nov. 9, 1945; Rabinowitch et al., New Piles Meeting, Report CF-3352, Oct. 16–17, 1945.
17. H. F. McDuffie, Possible New Reactor Types, Report Y-F18-3, Aug. 25, 1950.
18. Criticality and Control: Technical Report No. 6, Fairchild Engine & Airplane Corp., Report NEPA-6 October 1948; T. R. Mitchell, Critical Masses in Operable Air-cooled Beryllium Carbide Moderated Reactors, Report NEPA-1263, June 10, 1950; Myron A. Coler, Homogeneous and Circulating Fuel Reactor, Report TAB-88, Aug. 3, 1950.
19. A. S. Thompson and T. Fahrner, Design Study of a Low Power Research Reactor, Report NAA-SR-34, Oct. 14, 1949.
20. Classified Progress Report of the Reactor Science and Engineering Department, Brookhaven National Laboratory, Report BNL-67, June 1950; D. W. Bareis, Liquid Reactor Fuels: Bismuth-Uranium System, Report BNL-75, September 1950.
21. Progress Report for July 1950, Battelle Memorial Institute, Report BMI-P-31; R. I. Jaffee et al., Gallium in Nuclear Reactors: Use as a Primary Coolant, Report BMI-T-17, Aug. 1, 1949.
22. W. R. Grimes et al., High Temperature Fuel Systems, Report Y-657, July 20, 1950
23. H. R. Stephan, Properties of Various Liquid Coolants, Report NEPA-IC-50-4-20, Apr. 10, 1950.

December 1950

C45

DECLASSIFIED

On the Hazard Due to Nuclear Reactors

By M. M. Mills

Atomic Energy Research Department
North American Aviation, Inc.
Downey, California

Report NAA-SR-116 (Del.)

ABSTRACT

A major hazard associated with any nuclear reactor is the possible contamination of the atmosphere or water supply by the accidental release of the radioactive materials contained within the core. This problem can be considered in two stages: (1) the technological sequence of events leading to the hazardous release of radioactive materials from the reactor, and (2) the distribution of this radioactivity by meteorological and hydrological mechanisms. The second problem is not considered here since it is treated adequately elsewhere.[1-21]

The possible mechanisms of reactor catastrophe are mechanical disruption, cooling failure, and reactor runaway. Sabotage seems to be the most probable cause of mechanical disruption. On the basis of the theoretical studies which have been carried out, cooling failure and reactor runaway seem to lead to the same type of behavior. This is the gradual, nonexplosive release of volatilized substances containing radioactive products, and the quantity so released is usually small enough to be contained within an adequately sealed building. Some experimental studies are needed to substantiate these theoretical conclusions.

It appears likely that for the reactors which have been built or are presently contemplated an adequately gas-tight reactor building can remove the public hazard. The absence of mechanical shock, external to the shield, makes this possible. Some development in building construction may be needed to attain this goal.

Studies, both theoretical and experimental, leading to intrinsically safe designs would be very desirable. The possibility of building a reactor which is intrinsically safe because of a large negative transient temperature coefficient is demonstrated with an example.

INTRODUCTION

Scope

A radically new hazard has come with the technical development of nuclear reactors. The radioactivity contained in the core of a power reactor can amount to more than a billion curies of fission products, and there may be also substantial amounts of other materials such as plutonium.

For example,[1] if all the radioactivity in a 250-megawatt reactor were released, a surrounding area

714 046

DECLASSIFIED

10 miles in diameter might be subject to such intense irradiation that some 15 per cent of the population would receive a fatal dose. The catastrophic nature of such a release of radioactivity in the center of a large city is obvious. Similarly, if 1 million curies of radioactivity is released into the waters of a major watershed [the flow of the Missouri River at Sioux City, Iowa, (see Appendix D of reference 1)] over the period of a year, the resulting water will have just about tolerance radioactive contamination. Only 750 grams of plutonium is enough to contaminate one square mile of watershed to the tolerance limit for 30 years (see Appendix C of reference 1). The important point here is the public hazard; an accident with one reactor could force the evacuation of a large city or the temporary abandonment of a major watershed.

This problem of public hazard may be considered in two steps: (1) the mechanisms by which radioactive or other poisonous materials are released from the reactor and (2) the manner in which these materials might be dispersed over the surrounding areas. One viewpoint, which is conservative but, in the writer's opinion, is unduly pessimistic, is to assume that the radioactive material within any reactor will always somehow be released. The problem of examining the hazard presented by the reactor is then simply to study the meteorological and hydrological conditions at any proposed reactor site, taking note of the proximity of major population centers or strategic installations. A substantial amount of study has been given this problem of radioactive dissemination (references 1, 8, 13, 14, 16, and 18), and no additional study is contemplated here. The main interest in the following discussion will be to investigate mechanisms by which radioactive materials might be released from the core of a nuclear reactor and to discuss design techniques which will eliminate or minimize this possibility.

Operations hazards such as danger to the operating crew or strategic cost if a reactor is destroyed will not be considered. The operational hazards of a more or less conventional type, chemical and fire danger, mechanical failure, and corrosion, will not be discussed in detail. They are important and difficult problems in any reactor design but are not of primary interest here since they fall in or near fields of conventional technology. These problems are discussed elsewhere.[16]

Possible Accidents

The technological sequence of events leading to the escape of radioactive material from the core of a nuclear reactor will be referred to as "reactor catastrophe." There are several ways in which this may happen:

(1) Mechanical disruption in which the reactor structure may be damaged by accident, sabotage, or acts of God, e.g., earthquake. There are adequate design techniques known to protect against acts of God, except, perhaps, the very unlikely possibility of a direct hit on a reactor by a large meteor. This leaves only accident and sabotage to be seriously considered.

(2) Cooling failure in which the reactor structure may be sufficiently damaged by overheating due to failure of the cooling system to allow fission products to escape. Because of delayed power production due to fission-fragment decay activity, this may happen even if the reactor is shut down at the instant of cooling failure. The problem is more serious if cooling failure follows runaway behavior of the reactor.

(3) Reactor runaway in which, if the control system fails or accident or sabotage occurs, a release of excess reactivity (excess k) may lead to a rapid power-level increase, which may only stop after self-induced melting, disruption, or mutilation of the reactor. In some instances intrinsic temperature or power coefficients may be adequate to prevent serious damage of this sort. Techniques designed to incorporate such protective coefficients in the behavior of the reactor are desirable.

REACTOR CATASTROPHE

Sabotage and Disruptive Accidents

At this point, the problems of sabotage and disruptive accidents may be discussed briefly. A serious treatment will require much more study than is contemplated here.

The problem of sabotage is serious, and study by the Reactor Safeguard Committee[1] has indicated that during wartime sabotage and attempted sabotage are quite prevalent. However, effective sabotage of a nuclear reactor is not easy. There are essentially three methods: (1) The saboteur may induce a reactor runaway. The analysis of the behavior of a runaway reactor will be studied in detail below and will not need further technical consideration here. To effectively initiate a disruptive runaway the saboteur would have to be someone with considerable technical competence in a position of trust. Designing the reactor so that the efforts of many people, under skilled technical guidance, for an extended period of time would be required to initiate a runaway would minimize the possibility of sabotage of this sort. (2) The saboteur may make use of materials present in the reactor to cause disruption of its structure. Getting water into a sodium-cooled reactor can serve as an example. Here the result of sabotage will be similar to what might happen if an ordinary accident were to occur. Such accidents are briefly discussed below. (3) The saboteur may attempt to disrupt the reactor by means of ex-

DECLASSIFIED

plosives. The massive shield (10 ft thick) of steel and concrete will require a substantial quantity of explosive for effective disruption, and the possibility of bringing this to the reactor without detection would seem unlikely. A more extended discussion of reactor sabotage may be found in references 1, 3, and 4.

A saboteur may also take radioactive or fissionable material from the reactor to be used as a weapon. After a short period of operation, the radioactive level of materials within the reactor would make such removal without detection quite difficult.

Disruptive accidents which occur because of cooling failure or reactor runaway will be discussed later. A brief mention of possible accidents from other sources, such as chemical reaction, is appropriate here. Although the total energy release from such accidents could be quite large, the rate of energy generation will probably be slow relative to the rate which would occur with conventional explosives. The materials now being used or planned for use in reactors might lead to behavior which would correspond to a serious chemical fire, but this behavior would hardly correspond to an explosion. This problem must be studied for each reactor in detail. Furthermore, although this is not an easy problem, the fundamental background of conventional technology can be drawn upon. However, some of the materials, as well as their conditions of utilization, are novel and will require detailed study and development.

The use of sodium coolant represents a problem of this kind, and one safeguard has been the elimination of water from the reactor building. A number of detailed discussions of problems of this type for specific reactors may be found in references 13 to 21.

Cooling Failure

One way in which the reactor structure might fail and perhaps lead to the release of radioactive material is by overheating subsequent to cooling failure. A nuclear reactor differs from conventional machines in that there is substantial power production even after the reactor is shut down. This is due to the energy production from the radioactive decay of fission-product nuclei. Some details of radioactivity computations, based on a simplified formulation of Way and Wigner,[25,26] are given in Appendix A. The radioactivity may be expressed in power units, or, on the assumption made here that one decay event corresponds to 1 mev of energy, it may be expressed in curies. The magnitude of this radioactivity, following normal shutdown of a nuclear reactor, is indicated in Table 1.

Table 1 —Radioactivity After Normal Shutdown*

Time after shutdown, sec	Radioactivity from a previous steady power of 300 kw		Radioactivity from a previous steady power of 250,000 kw	
	Power, kw	Activity, curies	Power, kw	Activity, curies
10	12.9	2.1×10^6	11,000	1.8×10^9
10^2 (1.7 min)	8.0	1.3×10^6	6,800	1.1×10^9
10^3 (16.7 min)	5.2	8.4×10^5	4,300	7.0×10^8
10^4 (2.8 hr)	3.3	5.3×10^5	2,700	4.4×10^8
10^5 (28 hr)	2.0	3.3×10^5	1,700	2.8×10^8

*This includes only effects due to fission products; see Appendix A.

If a reactor runaway were to occur just before shutdown, the radioactivity indicated in Table 1 would be temporarily augmented up to a time given by the energy burst in the runaway divided by the normal power.

W. H. Zinn and his staff[7] have prepared an excellent condensed summary indicating the temperature rise in the reactor structure which would follow the combined event of simultaneous cooling failure and shutdown of the reactor. This temperature rise is due to the fission-product activity. In their study it was assumed that the fission-product energy would all remain within some appropriate portion of the reactor. This was done to take into account the facts that the heat will be largely produced in the fuel elements and that the fuel elements may have poor thermal contact with portions of the structure of large heat capacity. The heterogeneous reactors at Hanford and Chalk River are examples of this. The result of the analysis is given in Fig. 1. Some details of the study are indicated in Appendix A. As would be expected, rapid radioactive heat production and small heat capacity, which lead to rapid temperature rise, are associated with reactors of high specific power and high power density. For example, Fig. 1 indicates that the Materials Testing Reactor (high flux) will melt down within 10 min after cooling failure even though normal power production is shut down.

714 048

DECLASSIFIED

Evidently, the consequences of cooling failure can be quite serious. It would certainly be a great loss and serious catastrophe if such an accident were to occur. However, it is probable that such an event still can be subject to enough control so as not to represent a public hazard. Normal safeguards would include stand-by pumping power for the coolant circulating pumps, quantities of coolant available under gravity feed, and an integral, natural convection cooling system adequate to handle delayed power production. The latter arrangement is especially attractive. In addition, the time scale is long enough (10 min or more) so that some protective measures can be taken if suitable equipment is ready in stand-by condition. However, even if cooling failure does occur, it does not have to represent a serious public hazard.

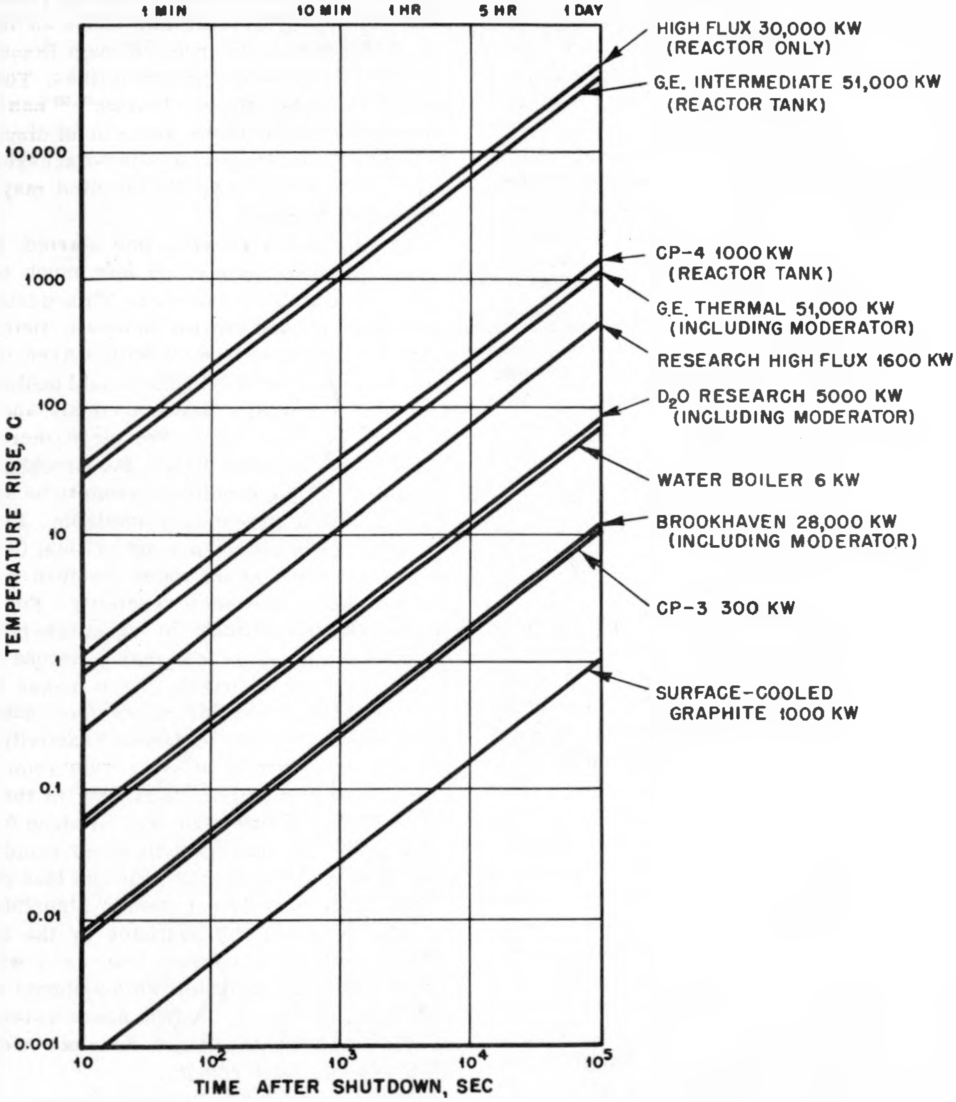


Fig. 1—Temperature rise after normal shutdown.

Structural failure following cooling failure will not be an event of explosive violence, although it may lead to the production of steam or it may induce serious secondary effects due to chemical reactions. As in the case of disruptive accidents, these secondary effects will be more like a bad chemical fire than an explosion. Furthermore, they can be studied before the reactor is built, and in some cases less reactive materials may be selected. If no disruptive secondary effects follow cooling failure, then the problem is

714 C49

DECLASSIFIED

easier. It is very unlikely, in any case, that there will be serious mechanical disruption of the shield. Moderate redesign of the shield, which is a massive structure for other reasons, should make it possible to prevent any major mechanical violence from escaping into the region external to the shield. If this is done, the provision of a suitable gas-tight reactor building should be adequate to prevent escape of radioactivity. This will be discussed in more detail below.

Reactor Runaway

A reactor runaway may occur if a nuclear reactor becomes supercritical by accident, negligence, or sabotage. The analysis of such problems must consider the degree of supercriticality that is likely to occur, factors that tend to accelerate or decelerate the runaway, and at what power level and total energy release the runaway is likely to stop. It turns out that accidents of this kind can be classified as dynamical or quasi-static, depending upon the reactor characteristics.

There are no direct or very complete indirect experimental studies which are applicable to the problem of reactor runaway.* The main result of theoretical studies, which will be outlined below, may be anticipated here. In no case does the runaway behavior of a nuclear reactor even remotely resemble the violence of an atomic bomb explosion. Furthermore, the description of a runaway as equivalent to so many pounds of TNT is also extremely misleading. Even the most violent runaway behavior of a fast-neutron-spectrum reactor is considerably less disruptive than a TNT explosion. In every case, in so far as violence arising from a runaway nuclear reaction is concerned, it appears that by proper attention to design of the shield no serious mechanical disruptive effects will propagate to the region external to the shield. Secondary effects such as chemical reactions and release of stored energy may still present serious problems but probably will produce effects nonexplosive in character.

There have been some rather detailed theoretical studies (references 1 to 5 and 15 to 17) of the problem of reactor runaway which will not be reproduced here. However, enough discussion will be given so that the meaning and scope of these studies may be understood.

(1) Initiation and Time Scale. A reactor runaway may be initiated by removal of the control rods (or insertion of reflector control rods), by addition of fissionable material or withdrawal of parasitic material from test facilities, by more effective assembly of the reactor (compression of the Los Alamos Fast Reactor), and by a sudden large decrease in coolant temperature in reactors with negative reactivity temperature coefficients. In the case of very-fast-spectrum U^{235} reactors, it appears that a thermal fluctuation could set off a spontaneous runaway. In this last case, local heating of the fuel may cause an improved fission absorption of neutrons through Doppler broadening of the resonance absorption lines. The details are rather intricate. Harvey Brooks[16,30] has given a criterion for such accidents and a brief discussion of the Doppler effect. A more detailed discussion of ways in which a runaway might be initiated may be found in references 5 and 17.

Granting that a runaway has started, the pertinent question is how rapidly and how much excess reactivity (excess k) is released. This question must be answered for each reactor in detail. Bethe[15] has estimated that the KAPL West Milton Area (KAPL WMA) Reactor under its fast loading could achieve an excess k of 0.01 essentially instantaneously and that 0.02 is probably an upper limit. For large thermal reactors (Hanford, X-10 at Oak Ridge, the Brookhaven Reactor) normal operating conditions seem to be such that only 1 to 2 per cent excess k is available. The Oak Ridge Reactor cannot exceed prompt critical (0.73 per cent), and by loss of coolant water Hanford might achieve about 2 per cent excess reactivity. For these large reactors it is difficult to visualize how reactivity changes can occur in less than a second or so. A detailed analysis[5] indicates that it makes little difference in these particular cases if an instantaneous or more gradual release of excess reactivity takes place. For reactors with xenon over-ride requirements and large excess reactivity available in the controls, a crude estimate indicates that, if about 0.02 excess k is reached, the runaway will be so rapid that no further motion of the control rods can take place.

For other reactors it seems plausible to assume the excess reactivity available in the controls is a measure of the maximum excess k which may be made suddenly available. This amounts to 1 or 2 per cent in many cases. Instantaneous release is a conservative assumption which does not seem to lead to unduly pessimistic results.

As a rough general criterion, an excess k of 2 per cent made instantly available seems to be satisfactory as a basis for estimating the behavior of runaway accidents.

After the runaway has been initiated, the power level of the reactor will increase approximately as $e^{t/\tau}$ where τ is the e-folding time for power rise. As a rough approximation it is given by

$$\frac{1}{\tau} = \frac{\Delta k}{\tau_0} \qquad (1)$$

---

*The atomic bomb is not included in the nuclear reactors considered here. The reactors of immediate concern are those described in references 1 to 21.

DECLASSIFIED

where Δk is the excess reactivity (in fractional units, not in per cent) and τ_0 is the neutron generation time (the time it takes the average neutron to be absorbed or leak from the reactor). For reactors of rather low multiplication, say low k_∞, a fairly general function giving τ as a function of τ_0 and Δk may be computed taking into account the effect of delayed neutrons. The results of computations[22] based upon U^{235} delayed neutrons* are shown in Fig. 2. The value of τ_0 may vary from a few milliseconds for large thermal reactors to microseconds for fast-neutron-spectrum reactors. Typical values of the e-folding time for 0.02 excess k are [redacted] 0.04 sec for the Argonne CP-3 Reactor, 0.004 sec for the Los Alamos Water Boiler, and 20 μsec for the KAPL WMA Reactor (fast loading). These times are all short compared to human reaction times. If the automatic control and safety devices do not function, the runaway will run its course.

(2) Runaway Behavior. After a runaway has been initiated, the energy which accumulates in the reactor may serve to further accelerate or retard the rate of power rise. Temperature coefficients, poison depletion, and, in liquid-core reactors, bubble formation are such effects. If these changes in reactivity are large and negative, the runaway may stop itself without serious harm to the reactor or danger to the surrounding area. Such large negative transient reactivity coefficients would furnish valid intrinsic protection of the reactor and are very desirable. If coefficients do not stop the runaway, it will continue until self-disruption or mutilation of the reactor stops it. If the reactivity changes induced by the runaway are positive, the reactor will be called "autocatalytic." Clearly, autocatalytic reactors are particularly unsafe.

Reactivity Coefficients. The problem of runaway analysis is further complicated by the fact that the reactivity coefficients during the transient conditions of runaway will usually be different from those corresponding to steady-state operation. In some cases it is quite difficult to estimate appropriate transient coefficients from steady-state measurements. Temperature coefficients may serve as an example.

In a reactor there are usually a variety of temperatures such as fuel, moderator, structure, and coolant temperature. In thermal reactors the temperature of thermal neutrons may also be considered. Even under steady-state conditions all these temperatures may be, and usually are, different. Under transient power rise, the fuel may heat up with only a minor change in other temperatures. For the KAPL WMA Reactor the time for the fuel to achieve thermal equilibrium with the coolant is about 0.02 sec. However, the e-folding time for runaway power rise may be as short as 20 μsec, and it must be concluded that essentially all the heat generated in the fuel elements will remain there. [redacted] Only in truly homogeneous reactors such as the Los Alamos Water Boiler will the temperature rise of fuel and moderator be the same.

[redacted] The temperature coefficient for the Low Power Research Reactor[9] has been estimated to be about -2×10^{-4} k/°C, due mainly to increased leakage from increased neutron temperature. Because this reactor is homogeneous, the coefficient should be effective during transient conditions. Details are given in Table 7.

The major poisons are produced as decay products of rather long-lived (lifetime on the order of 1 hr) mother nuclei. A runaway accident will last only a few seconds. Consequently, during a runaway poisons will not be in equilibrium and will usually undergo depletion leading to an autocatalytic effect. The magnitude of this effect has been estimated for a number of cases,[5] and fortunately it seems to be small. However, this must be reconsidered for new reactors.

The effect of bubble formation in liquid homogeneous reactors seems to furnish an intrinsic negative protective coefficient. Whether or not these bubbles are truly effective under transient conditions will depend upon their rate of nucleation and growth. The information available on this problem is largely theoretical,[36,37] although studies being made in connection with the Homogeneous Reactor Experiment should help to clarify this.[20,21] Experiments with transiently heated solutions would give direct information on this.

Experiments to determine the transient fuel temperature coefficient of enriched fast-spectrum reactors will require careful interpretation. A laboratory experiment which might employ a critical assembly and electrical heating of the fuel will lead to thermal expansion which can affect the statistical weight and degree of self-shielding of the fuel. Fast-spectrum

---

*The fraction of delayed neutrons, which may be taken as an indication of the division between delayed critical and prompt critical, is 0.0073 for U^{235}, 0.0047 for Pu^{239}, and 0.0024 for U^{233}. The larger fraction of delayed neutrons for U^{235} makes it more attractive from the viewpoint of control and safety.

DECLASSIFIED

reactors can have such a short e-folding time that heating of the fuel during runaway can take place without the same type of expansion of the fuel, since expansion of the core structure can take place only after the surrounding structure (blanket and reflector) has been pushed back. Expansion during a runaway is essentially limited by the speed of sound.

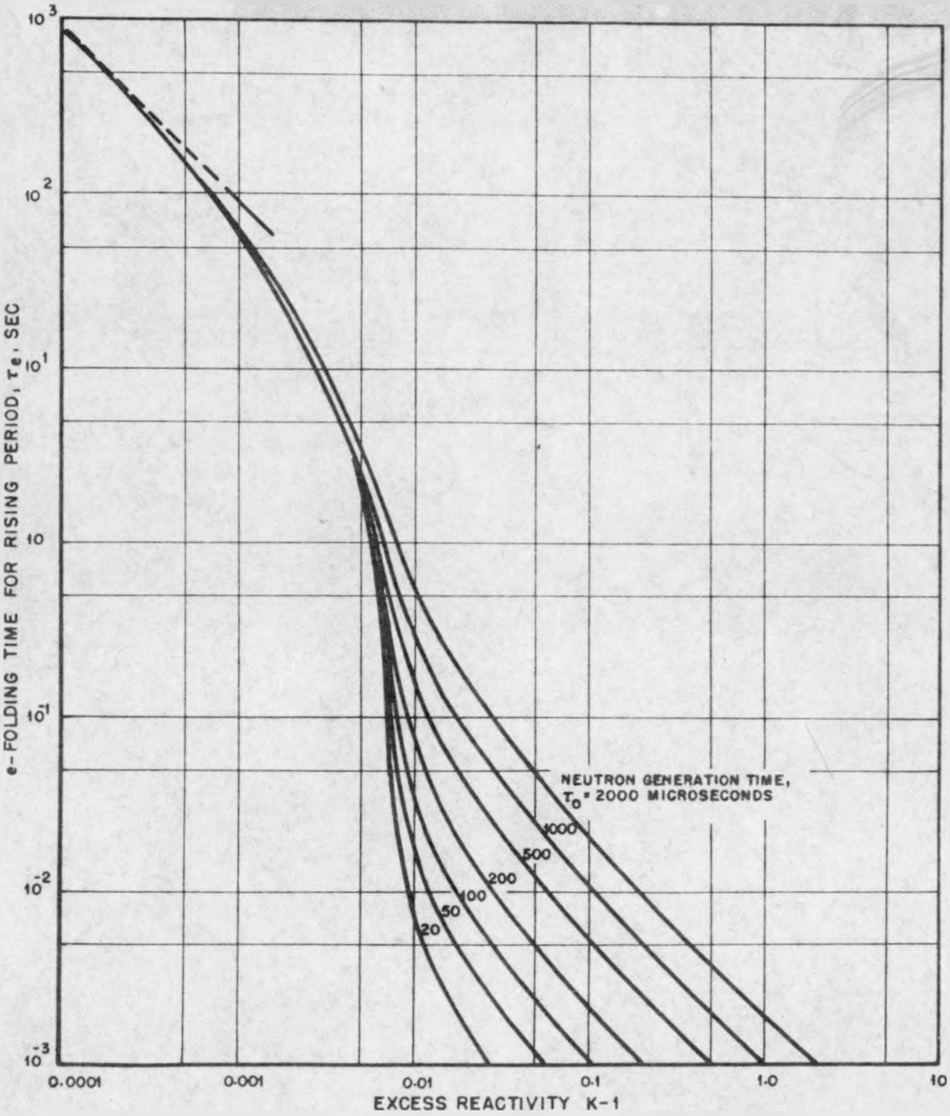


Fig. 2 — Variation of rising period, τ_e, with excess reactivity from the inhour equation

$$k - 1 = \frac{\tau_0}{\tau_e} + k \sum_i \frac{\beta_i \tau_i}{\tau_e + \tau_i}$$

The reactivity coefficients are discussed in more detail in references 2, 5, and 16.

[redacted]

[redacted]

[redacted]

(3) Termination of the Runaway. The violence and total energy release of the nuclear reaction up to the termination of the runaway is of immediate concern

DECLASSIFIED TID 052

here. The character of the stopping mechanism depends upon the relation between the nuclear and mechanical time scale of the reactor and may be classified as dynamical or quasi-static.

(a) Dynamical Accidents. The analysis of dynamical accidents and the detailed reasons for the classification are given in Appendix B. In general, the runaway will be dynamical in character if

$$R \gg c\tau \tag{2}$$

where R is a representative length associated with the core of the reactor. In spherical reactors it would be the core radius, and in reactors of compact design it may be taken as the radius of an equivolume sphere. The quantity c is the speed of sound in the reactor core, and τ is the e-folding time for power rise. The value R/c may be recognized as a mechanical time scale of the reactor core; Eq. 2 indicates that dynamical characteristics are the important controlling factors if the e-folding time is much shorter than the mechanical time scale. In particular, pressure generation and expansion of the core structure will not be able to keep step with the nuclear reaction.

The detailed analysis indicates that the fuel or core material will be vaporized or even partly ionized and that pressures large compared to the strength of core material will be encountered. Consequently, the detailed analysis of structural behavior need not be attempted when making estimates of energy release in a dynamical runaway. This makes it possible to derive the general formulas (cf. Appendix B) given below to describe the accident.

The maximum expansion velocity at the core-reflector interface is approximately given by

$$u = \frac{1}{n}\,\Delta k\,\frac{R}{\tau} \approx \frac{1}{n}\,\frac{R}{\tau_0}\,(\Delta k)^2 \tag{3}$$

where u = the expansion velocity
R = the effective core radius
τ = the e-folding time
τ_0 = the neutron generation time
Δk = the excess reactivity
n = a numerical factor on the order of unity (range from 0.5 to 2.0)

The maximum pressure generated by the runaway is approximately

$$p = \frac{1}{3n}\,\Delta k\;\rho\left(\frac{R}{\tau}\right)^2 \approx \frac{1}{3n}\,\rho\left(\frac{R}{\tau_0}\right)^2(\Delta k)^3 \tag{4}$$

where p is the pressure generated in the core and ρ is the density of the core material.

The nuclear energy released is then estimated from

$$E = \frac{pV}{\gamma - 1} \tag{5}$$

where E is the energy released, p is the pressure (Eq. 4), and γ is the ratio of specific heats for the vaporized fuel or vaporized core material if the reactor is homogeneous.

The volume term, V, is the volume occupied by the expanded vaporized fuel or core at the end of the runaway, not the volume under normal conditions. If only the fuel is vaporized, it may occupy twice the fraction of core volume taken up under normal conditions. If the core is vaporized, in a homogeneous reactor, this factor will amount to about 10 per cent at most. For vaporized ionized uranium fuel the factor $1/(\gamma - 1)$ may amount to 4.5.

Bethe[17] has given a detailed discussion of a possible runaway that might be encountered with the KAPL WMA Reactor and which may be taken as an example of a dynamical accident. Important points are that: (1) Spontaneous runaway (see criterion given by Brooks[16]) and runaway induced by control-rod motion will be about the same. The reason for this is that the runaway proceeds so rapidly after prompt critical is reached that essentially no further control-rod motion

DECLASSIFIED

can take place. (2) Only in the fastest neutron-spectrum fuel loading would the WMA Reactor have both a positive transient fuel temperature coefficient and a positive net change in reactivity on going to high temperature. With other loadings, even if the temperature coefficient starts out as positive, it changes sign as the temperature increases so that eventually it exerts a slowing effect.

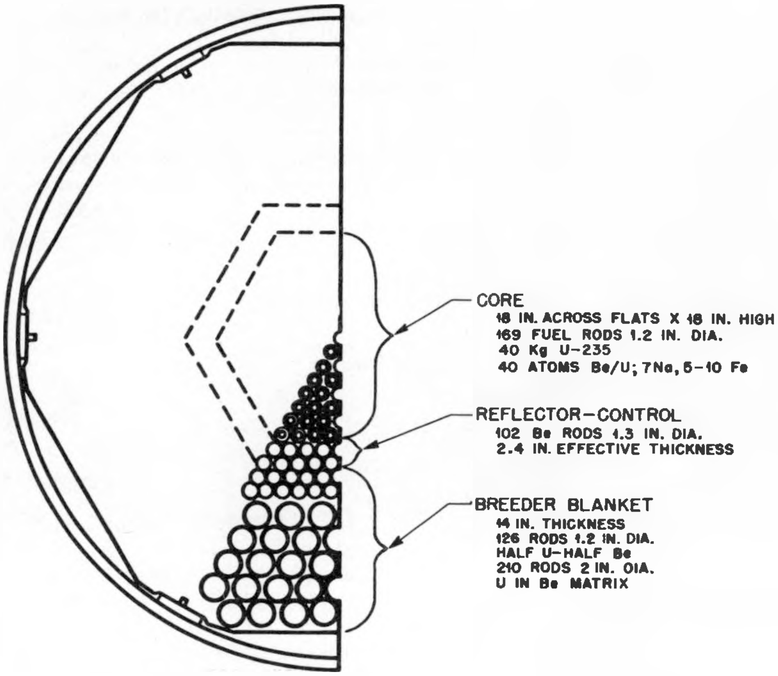


Fig. 4—General arrangement of the KAPL WMA Reactor.

The general arrangement of the KAPL WMA Reactor is indicated in Fig. 4. The violence estimate for runaway behavior of this machine is listed in Table 2. The results indicate a nuclear energy development of 44,000 kcal, a maximum pressure of 20,000 atm, and a maximum expansion velocity of about 44 meters/sec (98 mph).

The pernicious practice of describing nuclear accidents in terms of the equivalent amount of TNT has grown. This equivalence is based upon the energy generated in the accident and is completely misleading as a description of the violence. This is clearly shown in Table 2 where characteristics of a TNT explosion and the reactor accident are compared. The TNT pressure is greater than the reactor pressure by a factor of 9, and the TNT expansion velocity is greater than the reactor expansion velocity by a factor of 30. Indeed, the expansion velocity in the case of the reactor, 98 mph, looks much more like an auto accident than an explosion. The concept of the equivalent amount of TNT is misleading and should be abandoned.

Bethe[17] has studied the consequences of the runaway in some detail and has come to the conclusion that plastic deformation of the biological shield structure will absorb all the energy and will prevent mechanical shock from being transmitted to the reactor room. This is easy to see when it is realized that an average shield-temperature rise of 1°C or an average shield velocity of about 40 meters/sec is sufficient to absorb all the nuclear energy.

It is probable that a sodium fire will follow the accident. The energy that may be generated from the sodium in this way is about 30,000 kcal. It should be possible to install an automatic fire-control system to minimize the effects of such secondary fires.

The final outcome of a dynamical runaway of this kind will certainly be disagreeable. The reactor will be destroyed, the interior portion of the shield will be damaged, and there may be a serious chemical fire in the reactor room. This is indeed a serious event, and it is not the intention to minimize it here. The main concern here is possible hazard to the public. The theoretical conclusions that the runaway does not resemble an explosion and that no mechanical shock penetrates the shield are certainly very encouraging. The reactor room can be made gas-tight to control the spread of radioactivity, and the installation of automatic and auxiliary fire-control equipment should be effective, since the equipment would not be subject to serious mechanical shock.

Before considering quasi-static accidents, an estimate of the maximum possible nuclear-reactor runaway violence will be given. The results are listed in Table 3. This estimate was the outgrowth of an attempt to put an upper limit on the violence of a runaway for any nuclear reactor which produces appreciable power in normal operation. Because of the pessimistic nature of the assumptions, the runaway performance does resemble an explosion. It is unlikely that a reactor of this character will be built in the near future.

Table 2—Estimate of Runaway Violence for KAPL WMA Reactor (Fast-spectrum loading)

Assumptions

Neutron generation time, τ_0	0.4 μsec
Excess reactivity (mainly due to high temperature of fuel), Δk	0.01
Reactor e-folding time, τ	40 μsec
Velocity of sound in core, c	2×10^5 cm/sec
Effective core radius, R	27 cm
Density of core, ρ	4 g/cc
Stopping parameter, n	1.5
Fraction of core volume occupied by expanded fuel	0.25
Specific heat factor, $1/(\gamma - 1)$	4.5

From this $R/c\tau = 3$ (just barely a dynamical accident)

Results*

	Reactor†	Equivalent TNT
Nuclear energy to termination	44,000 kcal	44,000 kcal
Equivalent quantity of TNT	100 lb	100 lb
Maximum pressure	20,000 atm	180,000 atm‡
Expansion velocity	44 meters/sec	1,340 meters/sec
Heat of oxidation of the 6.8 kg of Na in core at 100 kcal/mole	30,000 kcal	

*Compare Eqs. 3, 4, and 5.

†The values given correspond to reference 17 for $\Delta k = 0.01$.

‡This includes impact pressure = density × (expansion velocity)^2, which amounts to about 30,000 atm.

(b) Quasi-static Accidents.

In general, the runaway will be quasi-static if

$$R \ll c\tau \qquad (6)$$

The symbols used here have been defined under Eq. 2. Under the conditions indicated by Eq. 6, mechanical effects may be treated by lumped parameters and by quasi-static methods. The pressures will usually be small, and the reactor will fail by "a weakest link" depending upon details of its design and structure. The mechanical shock from the nuclear reaction will be negligible, but the total energy release may be quite large, resulting from the heating of a large reactor mass. The equations (Eqs. 3 to 5) describing a dynamical accident may not be applied to quasi-static accidents. The energy analogy with TNT is even more misleading here than for the case of dynamical accidents. In most cases pressures will not exceed 10 atm.

The detailed estimates given in reference 5 and summarized below are probably as reliable as can be obtained without some experimental work. The analysis involves interactions between physical, chemical, mechanical, and nuclear systems, and the results must be considered tentative and approximate.

The probable stopping mechanisms for the reactors considered, Los Alamos Water Boiler, ORNL X-10 Reactor, and Argonne CP-3 Heavy Water Reactor, are listed in Table 4. The variety of mechanisms is apparent and may be contrasted with the simple expansion mechanism operating in the case of dynamical runaway.

C55

DECLASSIFIED

There are obviously no general formulas available which summarize the estimated runaway behavior for quasi-static accidents. Summarized results for the three reactors are given in Table 5.

Table 3 — Maximum Possible Nuclear Reactor Runaway Violence*

Assumptions	
Neutron generation time, τ_0	10^{-7} sec
Excess reactivity, Δk	0.03
Approximate e-folding time, τ	3×10^{-6} sec
Speed of sound in core (sodium and uranium), c	10^5 cm/sec
Radius of core, R	15 cm
Core density, ρ	10 g/cc
Stopping parameter, n	1.0
Specific heat factor, $1/(\gamma - 1)$	5
Fraction of core volume occupied by expanded fuel	0.5

$R/c\tau = 50$ (well into the dynamical region)

Results	
Nuclear energy to termination	2.12×10^5 kcal
Maximum pressure	2.5×10^6 atm
Maximum expansion velocity	1500 meters/sec

Equivalent TNT = 465 lb (analogy may be satisfactory)

*The assumptions were made by H. A. Bethe[2] and correspond to a very compact, heavily loaded U^{235} and sodium reactor.

In the examples given, initiation by a step-function increase in reactivity was assumed with $\Delta k = 0.02$. A detailed step-by-step analysis of the runaway was then made. The probable energy and gas volume released by the nuclear reaction and by secondary reactions triggered by the nuclear reaction are listed in the following order: A, probable; B, probable maximum; and C, improbable extreme. The theoretical estimate indicates that the runaway will stop between A and B, and rather nearer A. The values under C are believed to represent an upper limit.

Table 4 — Probable Runaway Termination Mechanisms

Reactor	Probable runaway stops	Probable nuclear energy release, cal
Los Alamos Water Boiler	By expansion of core, due to gas generation from fission-fragment decomposition of core fluid	10^5
ORNL X-10 Reactor	Probably by change in fuel-rod geometry when the uranium fuel rods melt, resulting in increased resonance absorption of neutrons	2×10^9
Argonne CP-3 Reactor	Mutilation of core structure when fuel rods fall to bottom of reactor tank after melting	10^8

Although the results so far available are theoretical and tentative, some conclusions may be given. Detailed studies[5] indicate that the quasi-static runaway is never of explosive violence. Secondary effects such as stored-energy release or chemical reaction will usually be a larger source of energy than the nuclear reaction. In reactors containing large quantities of water, there may be a fairly rapid pressure build-up which will probably be released as escaping steam jets before it reaches the magnitude of a steam explosion. In most cases it appears that there will be very little violence external to the shield.

This indicates that a suitable shield design with adequate internal expansion volume and adequate strength would serve to protect the reactor room. A sealed reactor room would then be a feasible method of preventing the spread of radioactivity and minimizing the public hazard.

SAFE DESIGNS

The *ideal safe design* would *result in* a reactor which is intrinsically safe and which is not dependent upon safety gadgets such as control circuits for protection. This is an important distinction. Teller has summarized this distinction by saying that the ideal safe design will be one which only a "Maxwell demon" can upset, while a mere "gremlin" can upset ordinary safety gadgets. Examples of such intrinsically safe characteristics are chemically nonreactive reactor components and large negative transient reactivity coefficients.

DECLASSIFIED

Table 5—Summary of Quasi-static Reactor Runaway Accidents

Remarks	ORNL X-10	Argonne CP-3	Los Alamos Water Boiler
Status	Built	Built	Built
Type	Thermal	Thermal	Thermal
Moderator	Graphite	D_2O	H_2O
Weight, g	2.24×10^8	6.40×10^6	1.36×10^4
Reflector	Graphite	Graphite	BeO
Weight, g	4.10×10^8	3.26×10^7	2×10^6
Total uranium, g	4.41×10^7	2.87×10^6	4.05×10^3
Uranium 235, g	3.15×10^5	2.05×10^4	5.80×10^2
Enrichment, % (0.71% is natural isotope mixture)	0.71	0.71	14.3
Power, kw	3.4×10^3	3×10^2	5.0
Cal/sec	8.14×10^5	7.17×10^4	1.2×10^3
Neutron generation time, sec	10^{-3}	5×10^{-4}	5×10^{-5}
Assumed excess reactivity	0.020	0.020	0.020
Corresponding e-folding time for power rise, sec	0.080	0.040	0.004
Assumed excess reactivity	0.016	0.017	
Corresponding e-folding time for power rise, sec	0.112	0.051	
Gross descriptions of catastrophe estimates			
Case A (probable)			
Energy generated in nuclear reaction, cal	2.34×10^9	0.15×10^9	1.02×10^5
Energy generated in chemical reaction, cal	5.00×10^9	1.74×10^9	
Release of stored energy	6.72×10^9		
Total energy	14.1×10^9	1.89×10^9	1.02×10^5
Gas volume released at NTP, cc	2.07×10^{10}	6.34×10^9	nil
Case B (probable maximum)			
Energy generated in nuclear reaction, cal	1.07×10^{10}	0.82×10^9	6.8×10^5
Energy generated in chemical reaction, cal	5.00×10^{10}	1.74×10^9	
Release of stored energy	6.72×10^{10}		
Total energy	12.79×10^{10}	2.56×10^9	6.8×10^5
Gas volume released at NTP, cc	2.07×10^{10}	8.46×10^9	nil
Case C (improbable extreme)			
Energy generated in nuclear reaction, cal	3.06×10^{10}	1.99×10^9	1.0×10^6
Energy generated in chemical reaction, cal	5.00×10^{10}	1.74×10^9	
Release of stored energy	6.72×10^{10}		
Total energy	14.78×10^{10}	3.73×10^9	1.0×10^6
Gas volume released at NTP, cc	2.07×10^{10}	11.23×10^9	8.5×10^5
Effective catastrophe parameters (Case A, step function, δk, only)			
Number of generations to end of catastrophe, $g = \ln [P(\max)/P(\text{normal})]$	10.2	12.3	
Effective value of $\tau_e e^g = E(\text{nuclear})/P(\text{normal})$, sec	2.88×10^3	2.1×10^3	78
Effective value of $\tau_e = E(\text{nuclear})/P(\max)$, sec	0.105	0.009	

714 C57

Safe Design Techniques

A number of design techniques which should minimize reactor hazards come readily to mind.[5] They may be classified according to possible catastrophic events: accident or sabotage, cooling failure, and reactor runaway. The brief discussion of sabotage which has been given will not be amplified here.

The possibility of accidents which are due to the chemical reactivity of reactor components, either with themselves or with the atmosphere, can be minimized by careful attention to design and construction of the reactor. Problems of this type can be adequately studied before the reactor is built, and they fall into the realm of chemical-engineering technology. Even pertinent radiation effects can be pretty well evaluated beforehand.

The ideal solution is the utilization of chemically nonreactive materials or materials which have already reacted (water and metal oxides).

The disastrous effects of cooling failure may be controlled by having suitable stand-by emergency cooling equipment available. Independently powered circulating pumps and large quantities of coolant available under gravity feed would give additional protection.

An attractive arrangement would be a natural convection cooling system since it is not subject to pumping power failure. In any case, the rate of temperature rise following shutdown is slow enough so that time (10 min or more) for some emergency measures will be available.

The effects of reactor runaway may be minimized by providing a suitable expansion volume inside the reactor shield, designing the shield as a physical barrier as well as a radiation barrier, and arranging automatic fire-fighting equipment in the reactor room. It should be possible to seal the reactor room to prevent the escape of radioactive products.

Intrinsic stability of the reactor, owing to large negative transient reactivity coefficients, is the ideal safeguard. Such a reactor cannot run away. An example of this type will be discussed below.

The possibility of achieving such an intrinsically safe design is dependent upon obtaining favorable reactivity coefficients. Some of these problems have been discussed in connection with reactor runaway. A systematic discussion of both reactivity coefficients and safe design techniques is given elsewhere.[5]

Example of Intrinsically Safe Design

The Low Power Research Reactor[9] is an example of a reactor designed to be intrinsically safe because of a large negative transient temperature coefficient. The reactor consists of an enriched-uranium-impregnated graphite core evacuated and filled to a few centimeters of helium pressure and contained within an aluminum tank. The core is surrounded by a graphite reflector. Cooling is accomplished by assembling the core from individually cooled fuel elements which are hexagonal blocks of graphite assembled on an aluminum tube through which coolant passes. The coolant is heavy water and was selected so the reactor would lose reactivity if the coolant were lost. The reactor is sketched in Fig. 5.

The general safety features of the reactor include: (1) Low power design so the build-up of radioactive fission products will be small. Through the use of enriched material, the flux is kept high at low power so the reactor is useful for research. (2) The reactor is thermal so the neutron generation time, τ_0, and therefore the time scale during an accident, is fairly long. (3) Impregnated graphite was selected rather than some homogeneous liquid arrangement so that the core would not have the dangers of fluid mobility or the problems of handling an efflux of radioactive fission-fragment gas. The gas can be absorbed in the graphite or contained in the evacuated core. (With a water-boiler arrangement the chemical decomposition products from fission-fragment bombardment of the solution constitute a large volume of gas which is difficult to dispose of, since it also contains radioactive gases.) The water-boiler arrangement does have the attractive feature of intrinsic stability (references 20, 21, 36, and 37). (4) Experimental facilities come up to, but not into, the core tank. This will reduce the statistical weight of these facilities and should improve the reliability of reactor control.

The essential safety feature is the large negative temperature coefficient originating in the homogeneous thermal character of the arrangement. In order to have a large temperature coefficient, the effect of 1/v absorption cross sections is exploited. As a matter of fact, the U^{235} fission cross section near thermal-neutron energy is believed to fall off somewhat more rapidly than 1/v. The neutron velocity is adjusted by heating the moderator. For transient effects to be controlled in this way, the fuel must be closely coupled to the moderator so that changes in power level will have an immediate effect on moderator temperature. This is accomplished by the homogeneous arrangement.

The characteristics of the reactor are listed in Table 6, and an indication of the basis of the temperature-coefficient estimate is given in Table 7.

The transient behavior has been estimated on the basis of a single-energy-group, one-delay period as follows:

$$\frac{dn}{dt} = \frac{\Delta k - \beta k_\infty}{\tau_0} n + \frac{c}{\tau_d} \tag{7}$$

$$\frac{dc}{dt} = \frac{\beta k_\infty}{\tau_0} n - \frac{c}{\tau_d} \tag{8}$$

$$\Delta k = \Delta k(\text{initially}) - r\alpha_T \int_0^t \left[\frac{n(t')}{n(0)} - 1\right] dt' \tag{9}$$

DECLASSIFIED

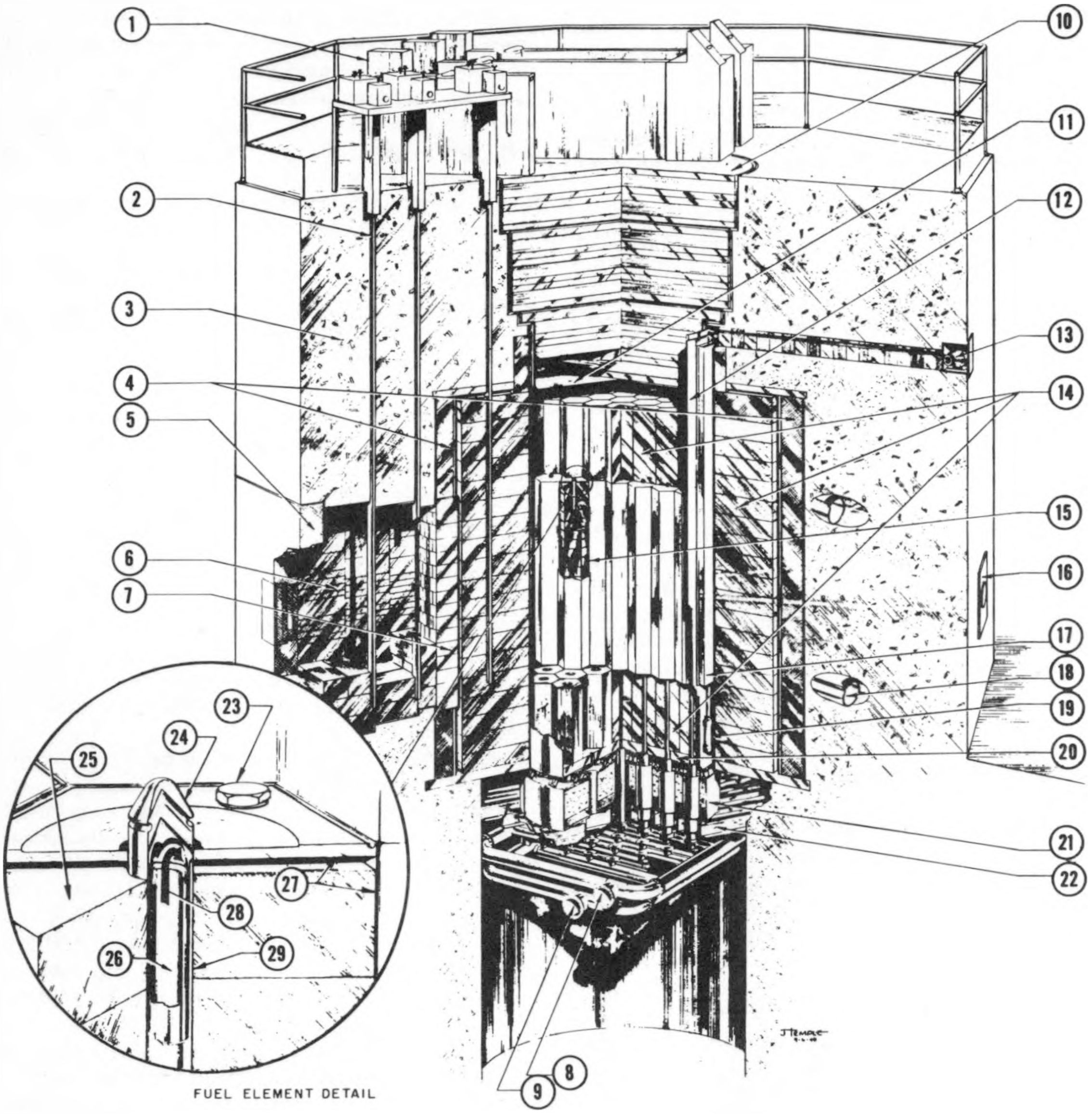


Fig. 5—General arrangement of the Low Power Research Reactor.

1. Pneumatic-tube terminal (3)
2. Multiple-specimen irradiation tube (6)
3. Concrete shield (high density)
4. Steel shield
5. Lead shield
6. Graphite thermal column
7. Bismuth shield
8. D_2O coolant out
9. D_2O coolant in
10. Iron-masonite shield (removable)
11. Top of core tank
12. Core tank (aluminum)
13. Rod operating mechanism
14. Graphite reflector
15. Core (showing fuel elements of stacked graphite-U_3O_8 fuel blocks canned in aluminum
16. Universal experimental hole (5)
17. Control safety rod sheath (4)
18. Instrument hole (2)
19. Rod stop
20. Bottom of core tank
21. Bottom shield
22. I-beam supports
23. Pump-out plug
24. Lifting lug
25. Graphite-U_3O_8
26. Inner aluminum tube
27. Aluminum can
28. Direction of flow
29. Outer aluminum tube

DECLASSIFIED

Table 6 —Characteristics of the Low Power Research Reactor

Core data	Mass, g	Volume, cc
U^{235}	3.2×10^3	
Graphite (fuel elements)	2.65×10^6	1.67×10^6
Aluminum (fuel elements)	0.104×10^6	3.84×10^4

Core contained within ⅛ in. thick aluminum can
Total heat capacity (fuel elements, no water) = 7.13×10^5 cal/°C
Power = 160 kw = 3.83×10^4 cal/sec
Power density = 50 kw/kg (U^{235}) = 95.8 kw/cubic meter = 2.29×10^{-2} (cal/sec)/cc
Uncooled, normal power level, rate of average temperature rise, $r = 5.37 \times 10^{-2}$ °C/sec
Normal average operating core temperature = 100°C
Multiplication constant, $k_\infty = 1.75$
Neutron generation time, $\tau_0 = 1.33$ m sec
Temperature coefficient of reactivity (see Table 7)
  Reflector effect factor = 0.737
  Factor for k_∞ = 0.430
  Factor for transient = 1.15
  dk/dT due to:
    Change in buckling by thermal expansion = $+0.047 \times 10^{-4}$/°C
    Change in L^2 by thermal expansion = -0.064×10^{-4}/°C
    Change in τ by thermal expansion = -0.087×10^{-4}/°C
    Change in L^2 by change in neutron temperature:
      Absorption = -1.830×10^{-4}/°C
      Scattering = -0.272×10^{-4}/°C
    Change in τ by change in neutron temperature = +0.189

Total steady state, $\alpha_T = -2.017 \times 10^{-4}$/°C
Total transient, $\alpha_T = -2.34 \times 10^{-4}$/°C

Table 7 —Temperature Coefficient for the Low Power Research Reactor

The steady-state temperature coefficient is computed from

$$\delta k/k = -\lambda_R \lambda_t \lambda_k \left(\frac{\delta\kappa^2}{\kappa^2} + \frac{L^2}{L^2+\tau}\,\frac{\delta L^2}{L^2} + \frac{\tau}{L^2+\tau}\,\frac{\delta\tau}{\tau}\right)$$

$$\lambda_R = \text{factor for reflector effect} = \left(\frac{a}{L_0+a} + \frac{L_0}{L_0+a}\,\frac{1}{1+\kappa^2 L_0^2}\right) = 0.737$$

a = equivalent spherical core radius = 70 cm
L_0 = effective relaxation length in reflector [includes a correction: tanh (thickness/true relaxation length)] = 45 cm
κ^2 = effective core Laplacian = $(0.032/\text{cm})^2$
λ_{k_∞} = factor for $k_\infty = (1 - 1/k_\infty) = 0.430$
$\delta\kappa^2/\kappa^2 = -1.57 \times 10^{-5}$/°C from thermal expansion
$\delta L^2/L^2 = +4.72 \times 10^{-5}$/°C from thermal expansion
$= +2.02 \times 10^{-4}$/°C from change in scattering with neutron temperature
$= +1.35 \times 10^{-3}$/°C from change in absorption with neutron temperature
$\delta\tau/\tau = +4.72 \times 10^{-5}$/°C from thermal expansion
$= -1.03 \times 10^{-4}$/°C from change in age with neutron temperature
$L^2 = 278.2\ \text{cm}^2$, in core
$\tau = 387\ \text{cm}^2$, in core

The transient coefficient will be larger in absolute value than the steady-state value as calculated above since the center of the core, a region of larger statistical weight, will undergo a larger temperature rise. This is given by a transient factor λ_t

$$\lambda_t = \text{core volume} \times \frac{(nv)^3\, d_{vol}}{\int (nv)\, d_{vol} \int (nv)^2\, d_{vol}} = 1.15$$

C60

DECLASSIFIED

In these equations n is the number of neutrons in the core and is proportional to the power density, and c is the number of latent neutrons contained in fission fragments. The latent neutrons are emitted with a delay period τ_d and constitute a fraction β of all neutrons; τ_0 is the neutron generation time; k_∞ is the intrinsic multiplication of the core; and Δk is the excess reactivity. The numbers r and α_T are the base heating rate (see Table 6) and the temperature coefficient, respectively. The integral in the last equation times α_T is the average temperature rise of the core. Judicious selection has yielded $\tau_d = 6$ sec and $\beta = 0.0065$ as appropriate values to approximate the complex five-delay periods. The equations have been integrated by numerical methods, and the results are shown in Figs. 6 and 7.

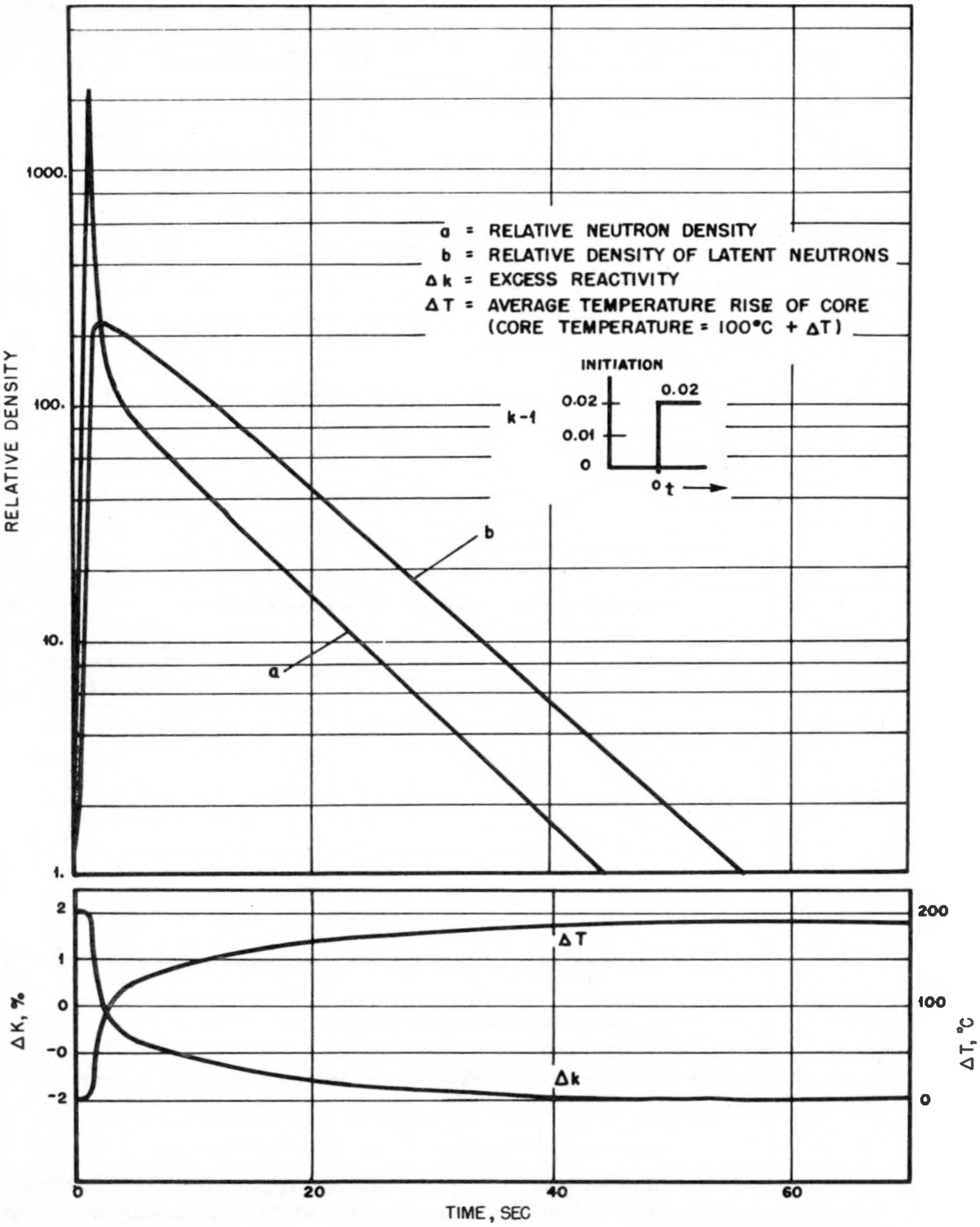


Fig. 6—Transient behavior of the Low Power Research Reactor.

(61

DECLASSIFIED

In Fig. 7 the variation of average core temperature with time after supercriticality is shown for step-function reactivity release of 2, 4, and 6 per cent. The initial core temperature was assumed to be 100°C. It is encouraging to note that even with 6 per cent excess reactivity runaway initiation, the average core temperature remains less than the melting point of aluminum. The reactor core is contained within an aluminum can (Fig. 5). Even at the maximum temperature achieved in an event of this type, the pressure of gases within the core will remain well below atmospheric pressure (the core was initially evacuated and filled with helium to a pressure of 1 cm or so), and, although the can may soften, it should still prevent escape of radioactive material from the core. The 6 per cent runaway initiation can certainly be considered an extreme example, and even in this case it is quite unlikely that radioactive material will escape from the core.

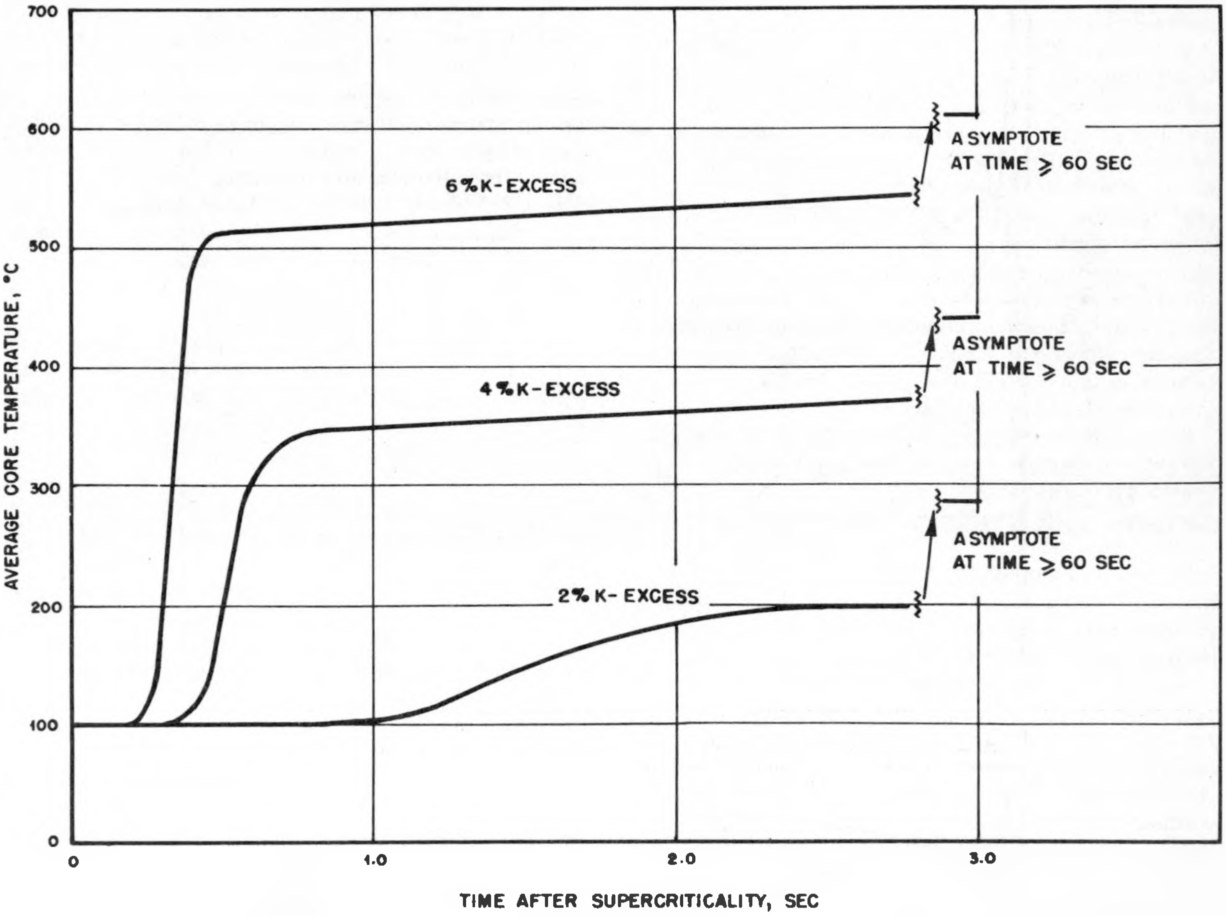


Fig. 7 — Temperature rise after supercriticality of the Low Power Research Reactor.

For the 2 per cent runaway it is unlikely that the cooling system will fail, and the reactor should eventually reach steady operating conditions. For the 4 and 6 per cent runaway examples, some of the heavy water in the cooling system may be vaporized. This may result in a pressure rise sufficient to cause minor damage to the coolant circulating system, but, in the event of loss of cooling water, the reactivity should decrease by about 1 per cent and supply an additional slowing effect on the runaway. The reactor arrangement is such that cooling-system failure will not lead to radioactivity release.

It may be concluded that this reactor is essentially safe against runaway owing to its large transient negative temperature coefficient. This is a fundamental, gremlin-proof protection not a safety gadget.

DECLASSIFIED

CONCLUSIONS

Reliability of the Conclusions

A number of studies of reactor hazards have been made[1-21] in an attempt to assess the potential dangers and to seek remedial measures. Most of these studies are theoretical in character, and, therefore, the final conclusions which will be summarized below must be considered as tentative and in need of some experimental verification.

There are many inexpensive experimental studies which would have a large effect on the reliability of the theoretical conclusions. The rate of bubble formation and growth in a boiling liquid heated throughout its volume,[37] the rate of chemical reaction of large lumps of molten uranium with water, and the rate of heat transfer across a solid-liquid interface under transient conditions are all examples of key studies which could be carried out on a laboratory scale without the need of a nuclear reactor. Recent results for the reaction of molten aluminum in water (see recent Argonne Quarterly Reports) give very encouraging results in that the reaction is apparently so slow as to present no chemical hazard.

In relation to reactor runaway, the most important and most obscure reactor characteristics are the reactivity coefficients.

Questions concerning reactivity coefficients could be clarified by further theoretical study and by carefully managed "flight-test" experiments in which a nuclear reactor is flashed and its performance is noted. These runaway experiments need not be carried to the point of damage to the reactor. It is probable that a full-dress destructive runaway experiment would never need to be run if the results of the other experiments can be successfully analyzed. Such a destructive test should certainly be postponed until some of the preliminary experiments outlined above have been completed. A systematic outline for combined analytical and experimental studies of reactor hazards is given elsewhere.[6]

In any case, reactor runaway behavior will usually involve complex interactions between nuclear, macroscopic physical, dynamical, and chemical systems. Conclusions given here on this problem must be regarded as tentative and approximate.

Conclusions

A nuclear reactor may be destroyed or damaged by sabotage, accident, cooling failure, or reactor runaway. Such dangerous and disagreeable behavior as structural failure by melting or vaporization of portions of the reactor core during runaway seem to be possible. An event of this type is serious enough in itself, involving the loss of a major reactor, but it may lead to the spread of radioactive fission products or other radioactive core material and constitute a hazard to a wide area.

In the studies relating to this problem, destructive accidents due to events other than reactor runaway can be considered as analogous to a serious chemical fire. They will be nonexplosive in character.

For the nuclear reactors which are now contemplated, the most violent reactor runaway will be an order of magnitude less violent than the explosion of TNT. In every case, suitable design of the shield with internal voids and adequate strength would prevent the transmittal of mechanical shock from the core into the reactor room. Secondary events triggered by the runaway nuclear reaction may lead to large energy generations from chemical reactions or stored energy (graphite) release. Although these secondary events may release more energy than the nuclear runaway, they will be nonexplosive in character.

The absence of mechanical shock external to the reactor shield suggests that it should be possible to prevent the spread of radioactivity by designing the reactor room or building so that it can contain any effluent from the reactor. The design of a sealed building, subject to some internal pressure, does not seem to represent an insuperable engineering problem.

The present reactor building, if sealed, would have to withstand a pressure rise of about 0.2 atm. This would require a stronger engineering structure than the present building. Construction practice indicates that for internal pressures of a few tenths of an atmosphere a surface structure is feasible, but for internal pressures exceeding 1 atm underground location will be more economical. The design and construction of a structure of this type will require a certain amount of development.

The utilization of a sealed reactor room, although not an intrinsic design characteristic, has been emphasized because it is very general and may be employed to palliate the potential hazard associated with any reactor. It can reasonably be expected that this approach will supply a considerable reduction in hazard, by minor engineering adjustment of the reactor structure and building, for even the high-power reactors planned for the future.

The possibility of achieving an intrinsically safe design has been illustrated by the Low Power Research Reactor. This ideal goal can probably be achieved for other reactors, but it is difficult to generalize on this point. A summary of the types of studies needed to develop and improve the safety of reactors is given elsewhere.[6] An important body of fundamental information could be obtained with simple, inexpensive studies. From the point of view of public hazard such an effort may not be needed if it is con-

C63

DECLASSIFIED

venient or necessary to place the reactors at a remote site for other reasons. However, remote location has nearly always resulted in impairment of technological development.

ACKNOWLEDGEMENT

The writer would like to thank the many scientists associated with the AEC reactor program for stimulating discussions of the hazard problem. He is especially indebted to M. Benedict, H. A. Bethe, H. Brooks, R. F. Christy, J. M. Dunford, D. Hall, J. Hall, B. Holzman, J. W. Kennedy, L. D. P. King, P. Reinker, F. Seitz, S. Siegel, C. Starr, E. Teller, G. L. Weil, A. M. Weinberg, J. A. Wheeler, E. P. Wigner, A. Wolman, and W. H. Zinn.

APPENDIX A

RADIOACTIVITY AND COOLING FAILURE

Radioactivity

The quantity of plutonium or special radioactive material in a reactor will depend primarily upon the type of fuel used (natural uranium, enriched material, or plutonium) and the amount of exposure of this material to the neutron flux. This problem must be considered separately for each reactor. On the other hand, fission-fragment radioactivity and the character of fission products are largely independent of the fuel used and may be determined conveniently by simple expressions, depending on the power history of the reactor. An analysis, due to Way and Wigner,[25,26] indicates that the production of sensible power by fission fragments can be described by the expression

$$p = p_0 \frac{E}{E_0} \left(\frac{\tau}{t}\right)^{1.2} - 10 < t < 10^7 \text{ sec} \qquad (10)$$

where p is the power released by fission fragments which were produced at time t = 0, with energy production E. The constants in this equation are $p_0 = 1.37 \times 10^{-2}$ kw, $E_0 = 1.0$ kw-sec, and $\tau = 1.0$ sec. Assuming the reactor has been operating for a long time at power level P and is shut down at t = 0, the production of power subsequent to shutdown may be found by integration to be

$$p = \frac{p_0}{0.2} \left(\frac{P\tau}{E_0}\right) \left(\frac{\tau}{t}\right)^{0.2}$$

or (11)

$$\frac{p}{P} = 0.069 \left(\frac{\tau}{t}\right)^{0.2}$$

If the reasonable but arbitrary assumption is made that radioactive energy production of 1.0 mev corresponds on the average to one decay event, then expressions analogous to Eqs. 1 and 2 may be written in which p is replaced by the activity a in curies and p_0 is replaced by $a_0 = 2.23 \times 10^3$ curies.

If a reactor has been operating for a long time at power level P followed by a very short period at very high power producing energy E just before shutdown, then Eqs. 1 and 2 may be combined to give

$$p = \frac{p_0}{0.2} \left(\frac{P\tau}{E_0}\right) \left(\frac{\tau}{t}\right)^{0.2} \left[1 + (0.2)\,\frac{E/P}{t}\right]$$

or (12)

$$\frac{p}{P} = 0.069 \left(\frac{\tau}{t}\right)^{0.2} \left[1 + (0.2)\,\frac{E/P}{t}\right]$$

The additional activity due to the burst of energy, E, decays away much more rapidly than the long-lifetime stored activity from long-term steady operation. At the end of a time E/P the radioactive power production is within 20 per cent of the radioactivity following normal shutdown.

Some numerical consequences of these expressions are listed in Table 1 of the text.

Cooling Failure

The analysis of W. H. Zinn and his staff[7] indicating the temperature rise which might follow cooling failure of a reactor even if accompanied by immediate shutdown is straightforward; the temperature rise is given by

$$\text{Temperature rise} = \frac{\text{radioactive decay energy release} - \text{heat losses}}{\text{appropriate heat capacity}}$$

The somewhat pessimistic assumption is made that the heat losses are negligible. The heat capacity involved may be less than the heat capacity of the entire reactor structure since for some reactors the fuel elements in which the fission-fragment energy is released may have only a weak thermal coupling to the large heat capacity of structural or moderating materials.

The radioactive decay energy released up to a time t after shutdown is given by integration of Eq. 11, and the final result for the temperature of the fuel element is

DECLASSIFIED

$$T(t) = T(0) + \frac{1}{0.16}\left(\frac{p_0\tau}{E_0}\right)\frac{P}{C}\,\tau^{0.2}\,t^{0.8} \qquad (13)$$

where C is the appropriate heat capacity, and T(0) is the temperature at the instant of shutdown. The temperature rise is proportional to the normal power level and inversely proportional to the heat capacity; it proceeds at a rate somewhat less than linear.

The results of an analysis of this type applied to a number of reactors have been given by Zinn[7] and are shown in Fig. 1.

APPENDIX B

MECHANICAL ANALYSIS OF REACTOR RUNAWAY

It is helpful to study the mechanics of a reactor accident in moderate detail in order to determine the severity of external effects.

The mechanical character of a reactor runaway may be qualitatively classified as (1) dynamical and (2) quasi-static.

(1) Dynamical accident requires a dynamical analysis with proper cognizance of the effect of sound velocity and other physical parameters. Stresses will generally exceed the strength of most or all of the materials from which the reactor is constructed, and a moderately reliable generalized formulation of a measure of the violence of the accident can be derived.

(2) Quasi-static analysis may be used in case the rate of power generation is slow relative to the velocity of sound in the reactor core. Pressures and stresses involved in this type of accident are usually quite low, smaller than the strength of many of the materials from which the reactor is constructed. The actual nature of the stresses will be determined by the engineering details of the reactor design. The failure of the structure, which stops the runaway, will be determined also by engineering detail and will occur by failure of the weakest link. The mode of failure cannot be described in general terms, but each reactor must be considered in some detail.

Dynamical Accidents

The discussion of dynamical accidents given here is due to H. A. Bethe,[2] who has studied also a number of refinements of the analysis.[17]

(1) Model and Analysis. In order that a general feeling for the character of dynamical accidents be gotten, a simple model consisting of a spherical core of radius R surrounded by an infinite incompressible reflector will be studied. Initially, both the core and reflector have the same and a uniform density (Fig. 8). The space variation of power density across the core will be neglected; a realistic estimate indicates that this is a reliable approximation.

The analysis may be broken into (1) the determination of the necessary expansion to stop the runaway, (2) the calculation of the rate of expansion and associated dynamical effects at the point where the runaway stops, and (3) the evaluation of total energy release and violence external to the reactor structure.

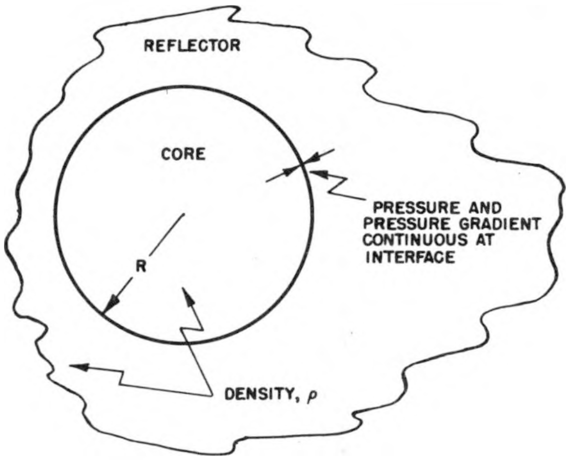


Fig. 8—Schematic reactor for runaway mechanics analysis.

(2) Required Expansion. The reactivity of the reactor will be measured by a parameter k denoting effective multiplication of the reactor assembly. This will depend upon k_∞, the intrinsic multiplication of the core material, a mean migration distance for neutrons, M, and the reactor size, R, by an expression of the form

$$k = \frac{k_\infty}{1 + A\frac{1}{R^2}M^2} \qquad (14)$$

where A is a constant depending on the detailed features of the reactor. Now

$$M^2 \sim \frac{1}{\rho^2} \qquad (15a)$$

where ρ is the density of the reactor material so that conservation of mass implies

$$\rho \sim \frac{1}{R^3} \qquad (15b)$$

Combining Eqs. 14 and 15a and b results in

$$k = \frac{k_\infty}{1 + BR^4} \qquad (16)$$

C65

DECLASSIFIED

Differentiating Eq. 16 yields

$$\Delta k = -4\left(1 - \frac{1}{k_\infty}\right)\frac{\Delta R}{R} = -n\,\frac{\Delta R}{R} \qquad (17)$$

The value k_∞ will be of the order of 1.5 or perhaps even 2 which gives

$$n \sim 1 \text{ to } 2 \qquad (18)$$

This n corresponds to the factor 3n in KAPL-294, Eq. 4.

(3) Dynamical Accident: Case I. (Pressures $\gg$ strength, $R \ll c\tau$.) Here the type of accident to be considered will be defined by the condition that the pressure generated should be large relative to the strength of the core and reflector materials and that sound should be able to cross the core many times during an e-folding period of power rise. The first condition makes it possible to neglect the strength (and therefore to a certain extent the details) of the materials in the reactor structure. The second makes it possible to assume that the generation of pressure and the expansion of the core and reflector material will proceed "in phase," the time variation being separable by a factor, approximately, $e^{t/\tau}$. It turns out that these two conditions are almost incompatible, so that Case I is a limiting case.

Let $x(r,t)$ = the position of a point, initially at the position r, at the time t (the Lagrangian coordinates*). The equation of motion is then

$$\frac{d^2x}{dt^2} = -\frac{1}{\rho}\frac{dp}{dr} \qquad (19)$$

where ρ is the density of material, and p is the pressure at the point r. In writing Eq. 19, explicit use has been made of the assumption that pressure $\gg$ strength; otherwise, additional terms would enter.

The boundary conditions are that the pressure should drop to zero at locations in the reflector far from the core and that at the core-reflector interface ($r = R$) the pressure and the pressure gradient (acceleration of a fluid particle) shall be continuous.

The main dependence may be estimated by splitting off solutions of the form

$$x = rf(t) \quad \text{in the core} \qquad (20)$$

This gives for the pressure variation

$$p = p_0\, e^{t/\tau}\left[1 - \lambda\left(\frac{r}{R}\right)^2\right] \quad \text{in the core} \qquad (21a)$$

$$p = p_0'\, e^{t/\tau}\left[\frac{R}{r} + \text{omitted}\left(\frac{R}{r}\right)^2\right] \quad \text{in the reflector} \qquad (21b)$$

Boundary conditions have been imposed in selecting the form of Eqs. 21a, b, and c. The continuity conditions at $r = R$ yield

$$\lambda = \tfrac{1}{3}, \qquad p_0' = \tfrac{2}{3}\,p_0 \qquad (21c)$$

Note that $p_0\, e^{t/\tau} = p_c(t)$ = the pressure at the center of the core. The equation of motion is now

$$\frac{d^2x}{dt^2} = +\frac{1}{\rho}\,p_c(t)\;2\lambda\,\frac{r}{R^2} \qquad (22a)$$

at the core-reflector interface $r = R$, and using the notation $x = X$, the equation becomes

$$\frac{d^2X}{dt^2} = +\frac{1}{\rho}\,\frac{2\lambda}{R}\,p_c(t) \qquad (22b)$$

Because of the exponential dependence, time integration merely multiplies by a factor τ. This gives

$$X - R = \frac{2\lambda}{\rho R}\,p_c\,\tau^2 \qquad (23)$$

Equation 23, true as a function of time, may be combined with the stopping condition (Eq. 17) by setting $X - R = \Delta R$.* This gives for $p_c(\max)$ at the stop of the runaway

$$p_c(\max) = \frac{1}{2\lambda n}\,\Delta k \rho \left(\frac{R}{\tau}\right)^2 \qquad (24)$$

Now

$$\frac{1}{\tau} = \frac{\Delta k}{\tau_0} \qquad (25)$$

where τ_0 is the neutron generation time (the effects of delayed neutrons are omitted). Inserting Eq. 25 into Eq. 24 gives

$$p_c(\max) = \frac{1}{2\lambda n}\,\rho\left(\frac{R}{\tau_0}\right)^2(\Delta k)^3 \qquad (26)$$

Equation 26 gives the "standard" result that the violence is proportional to the cube of the excess reactivity.

---

*This is the terminology of H. Lamb. Continental hydrodynamicists often reverse the terminology and refer to these coordinates as Eulerian.

*This assumes that the expansion of the reactor has no effect on reactivity until the runaway stops. It may be shown that this approximation introduces an error of about 15 per cent.

DECLASSIFIED

The validity of Eq. 24 may be checked by recalling that in a qualitative way strength is about 0.001 of the elastic modulus of a material. The elastic modulus is approximately ρc^2; Δk will be approximately 0.01; and $2\lambda n$ is approximately unity. These assumptions combined with the two inequalities defining Case I and Eq. 24 give

$$0.001\rho c^2 \ll p(\max) \ll 0.01\rho c^2 \tag{27}$$

This indicates the marginal character of the assumptions utilized in the derivation of Eq. 24. It is likely, in many cases, that, if $R/\tau \ll c$, pressures will be small compared with the strength. In the cases for which this is true, the detailed engineering features of the reactor must be known, although a quasi-static analysis may be followed.

(4) Dynamical Accident: Case II. ($R \gg c\tau$, pressure $\gg$ strength.) As in Case I, the assumption of pressures large relative to strength of the core and reflector materials indicates that a fluid mechanical analysis may be used. The assumption that sound cannot cross the core during the e-folding time for power rise indicates that pressures and displacements will not be in phase throughout the reactor structure, and explicit consideration of the time necessary for effects to propagate will have to be made. It will be assumed that the pressures will be small enough so that sound-wave, rather than shock-wave, analysis may be used.

From sonic theory the velocity of a fluid particle, u, is related to the excess pressures, p, by

$$p = \rho c u \tag{28}$$

where ρ and c are the density and speed of sound, respectively, in the reactor structure. The reactor will be assumed to shut down when an expansion, ΔR (Eq. 17), of the core actually does take place. The pressure at the edge of the core, $r = R$, will be somewhat less than the pressure in the center of the core. This factor will usually lie between ⅔ and unity and will be neglected in the present analysis. Since the pressure is rising exponentially, integration with respect to time merely introduces a factor τ. Integrating Eq. 28 yields

$$\int u\,dt = \Delta R = \frac{1}{\rho c} p\tau \tag{29}$$

or

$$p = \rho c \frac{\Delta R}{\tau} \tag{30}$$

Combining* this with the stopping conditions (Eq. 17) yields

$$p = \frac{1}{n} \Delta k\, \rho c \frac{R}{\tau} \tag{31}$$

Utilizing Eq. 25 gives

$$p = \frac{1}{n} \rho c \left(\frac{R}{\tau_0} (\Delta k)^2\right) \tag{32}$$

This indicates that the violence of a fast accident increases approximately as the square, rather than the cube, of the excess reactivity.

Equations 31 and 32 neglect the fact that the reactivity changes depend upon the average expansion of the core rather than expansion in the vicinity of the core-reflector interface. Since $R \gg c\tau$, it may be expected that only a part of the core has had time to expand so that Eqs. 31 and 32 are somewhat optimistic. The fraction of the core radius that has undergone expansion is $c\tau/R$, and this amounts to a volume fraction of $3c\tau/R$. Consequently, the change in reactivity corresponding to ΔR (Eq. 29) is smaller by this fraction than the value estimated in Eq. 17. The pressure generated may then be estimated to be greater by the reciprocal ratio giving

$$p = \frac{1}{3n} \Delta k\, \rho \left(\frac{R}{\tau}\right)^2 \tag{31a}$$

$$p = \frac{1}{3n} \rho \left(\frac{R}{\tau_0}\right)^2 (\Delta k)^3 \tag{32a}$$

These results are nearly the same as in Case I but with a somewhat lower coefficient ($\frac{1}{3}n \sim \frac{1}{3}$) rather than $\frac{1}{2}\lambda n \sim \frac{3}{4}$.

(5) Energy Generation. The energy generation may be estimated by the perfect gas equation

$$\frac{E}{V} = \frac{p}{(\gamma - 1)} \tag{33}$$

where E = the energy
V = the volume occupied by fuel at the end of the runaway [and may be quite different (larger) than the volume occupied by fuel under normal conditions]
γ = the ratio of specific heats, constant pressure/constant volume, of the vaporized fuel

---

*Equations 31 and 32 assume (1) no change in reactivity until reactor runaway stops and (2) an expansion ΔR at the edge of the core is sufficient to stop the runaway. The former introduces a 15 per cent error; the latter is discussed in the text.

DECLASSIFIED

p = the maximum pressure that is generated in the accident

The effect of fuel ionization on the energy (or the effective value of γ) must be considered if the estimated fuel temperature exceeds 10,000°K.

Quasi-static Accidents

In most cases, the conditions necessary for a quasi-static accident will be present if $R \ll c\tau$. Under this condition, the mechanical effects may be treated by lumped parameters and semistatic methods. The reactor will ultimately fail by a weakest link depending upon the details of its design and structure. The mechanical shock (except for possible chemical or stored-energy release) will be less than in the case of dynamical accidents, but the total energy release may be quite large, resulting from general heating of a large reactor mass. Here, the energy comparison with TNT, when used to estimate violence, is even more misleading than it is in the case of dynamical accidents. In most cases pressures do not exceed 10 atm.

Because the quasi-static accident depends upon the details of the reactor behavior, reliable estimates are difficult to make. The behavior of the reactor under runaway conditions depends upon an intricate interaction of complex nuclear, dynamical, physical, and chemical systems, and estimates are rough. Accurate estimates will probably require model studies and critical experiments.

REFERENCES

References 1 to 6 are survey reports of a fairly broad nature. Reference 1 is recommended as an over-all view of reactor hazards. References 6 to 12 cover special problems; references 13 to 21 cover specific reactors. In reference 17 many refinements in the theory of dynamical accidents have been worked out. Reference 21 discussed the homogeneous reactor and its potentially valuable property of self-regulation. Background material is discussed in references 22 to 39. The references on background are far from complete. They are inserted to illustrate the need for fundamental work on the cross sections of uranium, the behavior of multiplying lattices, and transient heat transfer problems.

1. J. A. Wheeler, J. W. Kennedy, M. Benedict, B. Holzman, A. Wolman, and E. Teller, Summary Report of the Reactor Safeguard Committee, Report WASH-3, July 1949.
2. H. A. Bethe, Minutes of Atomic Energy Commission Symposium on Reactor Hazards, issued by North American Aviation, Inc., Apr. 15, 1950.
3. J. V. Dunworth, Safety of Graphite Piles, Report AERE-NR-401, Sept. 2, 1949.
4. C. A. Rennie, Notes on Reactor Safety Conference, Report AERE-T/R-428, October 1949.
5. M. M. Mills, A Study of Reactor Hazards, Report NAA-SR-31, Dec. 7, 1949.
6. M. M. Mills, Program Study of Reactor Hazards, Report NAA-SR-70, Feb. 27, 1950.
7. W. H. Zinn, Considerations Regarding the Establishment of a Reactor Proving Ground for the AEC, letter from W. H. Zinn to G. L. Weil, Report ANL-WHZ-145, Apr. 22, 1948.
8. M. C. Leverett, L. W. Nordheim, and C. R. McCullough, Memorandum to E. P. Wigner on Hazards of Piles at Y-12, Report M-3335, Part I, Jan. 9, 1947, Part II, Jan. 22, 1947.
9. A. S. Thompson and T. Fahrner, Design Study of a Low Power Research Reactor, Report NAA-SR-34, Oct. 14, 1949.
10. W. C. Parrish, Transient Heat Transfer in Heterogeneous Reactors, Report NAA-SR-47, November 1949.
11. A. M. Weinberg, The Water Homogeneous Reactor, Paper 3, Session II, Information Meeting, Oak Ridge, Tennessee, October 24 to 26, 1949, Report TID-268.
12. M. M. Mills, The Influence of Safety Considerations on Reactor Development, Paper 4, Session II, Information Meeting, Oak Ridge, Tennessee, October 24 to 26, 1949, Report TID-268.
13. M. Benedict, H. Friedell, B. Holzman, E. Teller, J. Wheeler, A. Wolman, Report to the AEC on the Eleventh Meeting of the Reactor Safeguard Committee, Report WASH-23, June 30, 1950.
14. Report on the Brookhaven Nuclear Reactor prepared for the Reactor Safeguard Committee, Report BNL-18, June, and BNL-18 Supplement, August, 1948.
15. H. A. Bethe, Theory of Doppler Accident, Knolls Progress Report No. 19, February 1–29, 1949, Report KAPL-49.
16. H. Brooks, Safety of KAPL West Milton Area Reactor, Report KAPL-237, Nov. 28, 1949.
17. H. A. Bethe, Theoretical Estimate of Maximum Possible Nuclear Explosion, Report KAPL-294, Jan. 31, 1950.
18. S. McLain and R. K. Winkleblack, Hazards of the Materials Testing Reactor (supplementary report), Report ANL-SM-236, June 15, 1950.
19. S. McLain, Summary of Report to the Atomic Energy Commission on the Hazards of the Materials Testing Reactor, Report ANL-SM-516, June 15, 1950.
20. C. E. Winters and A. M. Weinberg, Homogeneous Reactor Experiment Feasibility Report, Report ORNL-730, July 6, 1950.
21. C. E. Winters and A. M. Weinberg, Report on the Safety Aspects of the Homogeneous Reactor Experiment, Report ORNL-731, Aug. 29, 1950.
22. D. J. Hughes, Delayed Neutrons, Report CF-3596, Feb. 1, 1946.
23. A. M. Weinberg and ORNL staff, Effect of Poisoning on Reactor Control (Xe cross section), Information Meeting, Los Alamos, New Mexico, May 6, 1949.
24. Analysis of U^{235} Cross Section Data, Reports KAPL-377, July 1950, and KAPL-394, August 1950.
25. K. Way and E. P. Wigner, Radiation from Fission Products, Phys. Rev., 70: 115 (1946).
26. J. K. Thornton and W. J. Houghton, An Influence Function for the Beta Activity of Uranium 235 Fission Products, Report NAA-SR-45, Sept. 1, 1950.
27. E. W. Bragdon, D. J. Hughes, and J. Marshall, The Eta Temperature Effect, Report CP-1381, Feb. 25, 1944.

DECLASSIFIED

28. A. C. G. Mitchell, L. Slotin, J. Marshall, V. A. Nedzel, L. J. Brown, and J. R. Pruett, Effect of Temperature on the Resonance Absorption of Neutrons by Uranium 238, Report CP-597, Apr. 22, 1943.
29. D. Hall and J. Hall, Search for Doppler Effect in U^{235}, Report LAB-P-5-31, 1948.
30. H. Brooks, The Doppler Temperature Coefficient of Uranium 235, Sec. V, Hazard Symposium, North American Aviation, Inc., Apr. 15, 1950.
31. E. P. Wigner, Resonance Absorption of Neutrons by Spheres, Report CP-4.
32. A. M. Weinberg, Fundamentals of the Chain Reaction, Project Handbook, Sec. E, Chapter IV, Report CL-697.
33. P. Morrison, Temperature Coefficient of the Reproduction Factor for Different Lattice Arrangements, Report CP-478, Feb. 19, 1943.
34. S. M. Dancoff, The Resonance Absorption Spectrum of Uranium, Report CP-1092, Nov. 24, 1943.
35. S. M. Dancoff and M. Ginsburg, Resonance Absorption in Lumps and Mixtures, Report CP-1589, Apr. 17, 1944.
36. J. A. Lane, The Bubble Problem in the Homogeneous Reactor, Report ORNL-728, Aug. 5, 1949.
37. M. S. Plesset, Rate of Formation of Vapor in a Uniformly Heated Liquid, Report NAA-SR-53, Oct. 24, 1949.
38. F. Kreith and M. Summerfield, Heat Transfer with Surface Boiling, Progress Report No. 4-68, Jet Propulsion Laboratory, California Institute of Technology, April 1948.
39. W. H. McAdams, J. N. Addoms, and W. E. Kennel, Heat Transfer at High Rates to Water with Surface Boiling, Report ANL-4268, December 1948.

October 1950

DECLASSIFIED

Production of a High-grade Uranium Precipitate from Ore Leach Solutions

By A. M. Gaudin, John Dasher, David Kaufman, Sara E. Bailey,
and Norman N. Schiff

MIT Mineral Engineering Laboratory
Watertown, Mass.

Report MITG-254

ABSTRACT

The recovery of uranium from Witwatersrand gold ores has received special attention both because of the probable future importance of these ores as a source and because of the difficulty caused by their very low grade (about 0.02 per cent U_3O_8). Several methods are described for the retreating of the low-grade precipitates from leaching solutions. These methods include (1) acid digestion, resulting in a 10- to 50-fold increase in uranium concentration, followed by peroxide precipitation, (2) carbonate leaching followed by acidification to remove carbonate and then by neutralization to precipitate a high-grade product, and (3) leaching with nitrated ether followed by neutralization with NH_3 to precipitate uranium hydroxide and ammonium nitrate and by a water leach to remove the latter.

Various methods are described for the removal of uranium directly from the leach liquor, the most promising being (1) reduction and pyrophosphate precipitation and (2) adsorption on strong-base anion-exchange resins. Pilot plants using the ion-exchange method are now in operation on the Rand.

INTRODUCTION

In a previous article[1] the early work of this laboratory on the recovery of uranium from low-grade ores was described. It was found that uranium minerals can be dissolved from low-grade ores or concentrates by dilute unheated solutions of sulfuric acid plus ferric sulfate if primary minerals or phosphates are present. The dissolved uranium may then be recovered by neutralization of the leach solution with lime, magnesia, or mixtures of them. The major impurities in the precipitate are iron oxides, alumina, silica, and gypsum, to the extent that lime is used. The proportion of these impurities can be decreased by partial neutralization of the pregnant solution before precipitation of the uranium. Air plus sulfur dioxide (from the pyrite in the ore) can be used for economical production of leaching reagents, although an auxiliary oxidant such as manganese dioxide is required.

The uranium precipitates obtained by neutralization were usually low grade and several methods were developed to retreat them. The most promising of these methods were (1) acid digestion and peroxide precipitation, (2) carbonate leaching, and (3) leaching with nitrated ether. Attention was also given to the selective removal of the uranium directly from the leach liquor, and the most promising methods were

DECLASSIFIED

(1) reduction and pyrophosphate precipitation and (2) adsorption of uranium on strong-base anion-exchange resins.

The purpose of this article is to describe these methods and another selective precipitation method involving copper and phosphate and to outline the steps leading to their development. Some of the lines of investigation which did not prove profitable will also be mentioned. Thus the previous article dealt largely with getting the uranium into solution or into a hydroxide precipitate while this article deals with methods of producing a medium-to-high-grade uranium product from these impure precipitates or leach solutions. Both articles are concerned mainly with the gold ores of the South African Witwatersrand because (1) these ores are extremely important and promise to provide a major source of uranium, (2) the problem of recovering uranium from leach solutions or precipitates is more difficult for these materials than for most other materials because the ores are very low grade (about 0.02 per cent U_3O_8), and (3) the major part of the effort of this laboratory has been on the Rand problem. However, examples obtained in the treatment of other ores will be included where available and pertinent. Discussion is restricted to sulfate leach solutions and precipitates obtained from them.

Table 1 — Analysis of Rand Leach Liquors* and Precipitate Assay

Material	Before neutralization, g/liter	After neutralization, g/liter	Precipitate, %	Barren solution, g/liter
U_3O_8	0.328	0.320	3.10	0.004
Fe	7.1	4.2	4.4	3.3
Mn	8.9	9.0	1.8	8.1
Al_2O_3	2.0	1.5	8.9	0.1
SiO_2	1.9	1.1	9.2	0.03
CaO	0.75	0.58	13.7	0.96
MgO	4.1	3.6	5.4	5.6
SO_4	59.4	42.5	34.8	37.7

*Cyanidation residue from the Blyvooruitzicht gold mine (0.024 per cent U_3O_8) was leached with 55 pounds of H_2SO_4 and 10 pounds of MnO_2 per ton of residue at pH 1.2, neutralized with 25 pounds of limestone per ton to pH 3.5, filtered, and washed with barren solution and then with water to minimize rejection of impurities in residue. The wash solution was used to repulp the next batch of ore. The pregnant solution was neutralized to pH 6.2 with 5 pounds of calcined dolomite per ton of residue. The precipitate, amounting to 10 g/liter of solution was filtered and dried. The build-up of impurities was intentionally made higher than normal by leaving only 10 per cent of the barren liquor in the residue filter cake. Under normal conditions a product containing 5 per cent U_3O_8 would be obtained.

The analysis of a Rand leach liquor with and without partial neutralization (pH 3.5), a precipitate obtained from the partially neutralized liquor by further neutralization with calcined dolomite (pH 6.2), and the resultant barren solution are given in Table 1.[2]

It may be noted that this precipitate contains only 3.1 per cent U_3O_8. For comparison the precipitates from leach liquors of Congo ores (feed 2 to 3 per cent U_3O_8) and from the cupriferous uranium ores (feed 1.6 per cent U_3O_8) from Capitol Reefs, Utah, assay 30 to 40 per cent U_3O_8.* These higher grade products are suitable refinery feeds, but the Rand precipitate must be upgraded or a more selective method must be used to recover uranium from the leach solutions.

RETREATMENT OF PRECIPITATES

Early Investigations

Attempts were made to redissolve Rand hydroxide precipitates in various acids in order to leach out the uranium and to obtain a more concentrated solution from which the uranium might be selectively precipitated. It was found that the uranium was easily dissolved in sulfuric, nitric, or hydrochloric acids but so were the iron and aluminum. Silica and gypsum were left largely undissolved. The silica in these solutions was in a gelatinous form so that the uranium solution could not be separated from the insoluble material by filtration; in fact, when strong acid was used, a gel was produced.

However, if the precipitate was treated with excess strong sulfuric acid and then heated to 250°C for half an hour, when the resulting cake was leached with water, the iron, aluminum, and uranium all dissolved and could be easily separated by filtration

---

*To obtain this grade of precipitate from Capitol Reefs leach liquor the copper must first be removed by cementation or electrolysis.

DECLASSIFIED

from the calcium sulfate and dehydrated granular silica. Roasting with inadequate quantities of acid resulted in some of the iron and aluminum being rendered water-insoluble along with a lesser, but appreciable, proportion of the uranium, but the filtration of this material was difficult. Roasting of the precipitate and subsequent leaching with acid allowed some selectivity in dissolving uranium away from the other impurities, but these pulps were also unfilterable, even though roasting had dehydrated the silica.

It was then found that, if the precipitate was leached with dilute sulfuric acid at pH 3.5 and digested for several hours near boiling, selective uranium extraction could be obtained and the impurities could be converted into a filterable form.[3] This was developed into the acid-digestion process described below.

While this method of selective dissolution of uranium from precipitates was being developed, experiments were run on some of the solutions obtained by less selective treatments using an alkali orthophosphate as a precipitant for the uranium. Before phosphate is added, ferric iron is removed by neutralization to pH 3.5. If ferrous iron is in the precipitate, it is oxidized with air before acid treatment. Tests on pure solutions[33] showed that uranyl phosphate could be precipitated at low pH, and British workers reported that on iron-free solutions obtained from low-grade precipitates the uranium could be precipitated at a pH of 1.8 if ammonia and sufficient orthophosphate to react with the uranium and to complex the aluminum were added. Four days were required for this precipitation.[4]

In the MIT precipitation work an attempt was made to improve the selectivity of the precipitation of uranium from aluminum by reducing the uranium to the tetravalent state. Tetravalent uranium is chemically similar to thorium; it forms precipitates in solutions too acid for uranyl compounds to precipitate. Uranium was selectively precipitated with phosphate from reduced solutions obtained by acid-leaching Rand precipitates, but the separation was not sharp, as an appreciable fraction of the aluminum accompanied the uranium. At this time one test was run on these solutions with pyrophosphate. Results were so much better that we were encouraged to try pyrophosphate precipitation of the whole leach liquor.[5] This was quite successful as will be described in the section of this paper dealing with selective precipitation.

Another likely method of getting the uranium from a low-grade precipitate involved leaching it with sodium carbonate. Preliminary tests gave encouraging results. Extractions were usually over 50 per cent and sometimes over 95 per cent, but results were not reproducible and variation of carbonate leaching conditions seemed far less important than the uncontrolled variation in precipitate composition.[6] Good extractions were obtained by acidifying the precipitate and running the slurry into a carbonate solution,[7] but further investigation showed this to be impractical.[8]

Meanwhile it was found that, while a large number of variables affected the amount of uranium extracted from precipitates with a single carbonate leach, good extractions were easily obtained under many conditions if multiple leaches were used.[9] This was developed into the carbonate leaching process described below.

Acid-digestion Upgrading Process

When a Rand hydroxide precipitate is agitated with enough sulfuric acid to give a pH of 3.5, most of the uranium is dissolved but the slurry is unfilterable because of gelatinous silica. If, however, this slurry is heated to 90°C and agitated at this temperature for 8 to 16 hr, recrystallization of some constituents seems to take place so that the slurry becomes readily filterable. This heat treatment therefore has two useful effects, rejection of silica and improved dewatering characteristics. Furthermore, at pH 3.5, of course, all the ferric iron is rejected to ensure complete rejection of iron. The ferrous iron which is present in the precipitate should first be oxidized by air. This air oxidation proceeds readily above pH 5.5, but it is disappointingly slow in acid mediums. Therefore since the oxidation of ferrous iron produces acid, care must be taken, and some alkali added if necessary, to maintain the pH above 5.5 during this oxidation step. If this is done properly, the digestion step removes all the iron. An unexpected dividend from the acid digestion was the rejection of most of the alumina. It is not known whether the aluminum forms a basic sulfate or a silicate.

The solution obtained from acid digestion is 10 to 50 times more concentrated in uranium than the original Rand leach liquor, and the total amount of other impurities has been greatly reduced. Practically all the iron and silica, and most of the aluminum, is rejected, but traces of other impurities like zinc and copper are concentrated with the uranium. An ammonia precipitation of this solution will give a product assaying about 30 per cent U_3O_8.

A number of other precipitants may be used with or without reduction, including phosphate, fluoride, and oxalate, but we preferred to use peroxide precipitation. Peroxide precipitation is reasonably complete at pH 2.5 to 3, a reduction is not needed, and the resulting precipitate contains over 90 per cent U_3O_8. Unlike the precipitates obtained with fluoride or phosphate, it required no further treatment.

In order to make peroxide precipitation complete it is necessary to make the solution 0.2M in peroxide. To do this precipitation economically therefore it is necessary to minimize the solution volume by recirculating wash solutions and by carrying out the acid

714 072

DECLASSIFIED

digestion in a relatively thick pulp. If this is done, the solution to be precipitated contains about 5 g of U_3O_8 per liter, and at this concentration the cost of peroxide is reasonable. A flow sheet for the process is shown in Fig. 1.

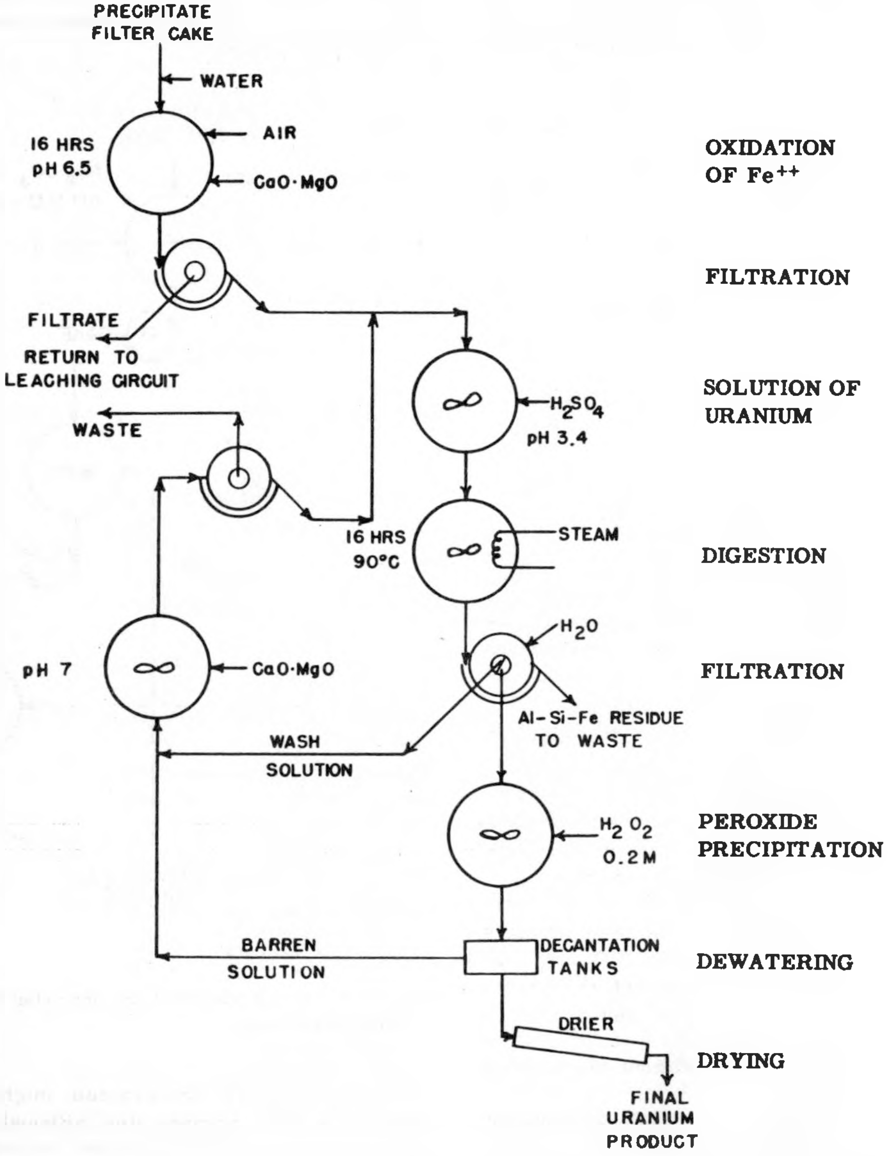


Fig. 1 — Flow sheet for acid-digestion upgrading process using peroxide as final precipitant.

The metallurgical results obtained are dependent on the composition of the primary precipitate treated. Typical results are summarized in Table 2.

On precipitates from simple leach liquors the uranium loss in the Al-Si-Fe product was 10 per cent, and on precipitates obtained after oxidizing all the ferrous iron before partial neutralization the loss was less than 2 per cent.[10]

Multiple Carbonate Leach

Carbonate leaching studies have indicated that the extraction of uranium from low-grade Rand precipitates is affected greatly by the conditions of the precipitation and the leaching. However, when three or four successive leaches were used on the same feed

714 073

with enough carbonate, over 95 per cent of the uranium was extracted from any precipitate. It was also found that the pregnant leach solutions from the second and subsequent leaches retained considerable dissolving power. Countercurrent leaching tests showed that only half as much carbonate is required to give adequate recovery as is required if no countercurrent procedure is used. As might be expected, the carbonate consumption was affected by the proportion of gypsum in the precipitate, but the gypsum was converted to calcium carbonate only in part. The carbonate consumption was also affected by the amounts of iron and aluminum present, presumably because they were partly present as basic sulfates. For best extraction it was found necessary to maintain a pH between 9.5 and 10. Essentially the amount of carbonate required was constant per unit of precipitate treated, and accordingly the economics of the process are directly dependent upon the grade of precipitate.

Table 2 — Acid-digestion Upgrading Process Using Peroxide as Final Precipitant*

Material	Amount, g/kg of ore	Assay, % U_3O_8	Distribution, %
Al-Si-Fe precipitate	5.07	0.09	3.9
Final U product	0.131	86.8	96.1

*Precipitates estimated to weigh 0.7 per cent of the primary feed to leaching. The feed to upgrading assayed 2.3 per cent and was obtained in a locked-batch cyclic test on Western Reefs cyanide residue (0.018 per cent U_3O_8) leached with reagents made by the SO_2-air process, neutralized with limestone to pH 3.5, filtered, and precipitated with calcined dolomite.

Studies were made of variations in leaching conditions, and it was found that in cyclic tests primary precipitates containing over 5 per cent U_3O_8 could be obtained if the pulp after leaching and before separation of the solution by filtration was neutralized to pH 3.6 to 3.8. In noncyclic operation neutralization could not be carried above pH 3.5 without appreciable loss of uranium.

Equivalent extractions in carbonate leaching of precipitates were obtained by using either a 24-hr leach at room temperature or a 0.5- to 1-hr leach at 90°C. If a hot leach is used, it is necessary to use pressure filtration, whereas at ambient temperature vacuum filtration may be used.

To remove uranium from the pregnant liquors they can be acidified to evolve carbonate as CO_2 and then can be neutralized with a hydroxide to give a high-grade-uranium product containing at least 40 per cent U_3O_8. Attempts were made to precipitate the uranium from the carbonate solution by raising the pH without intermediate decarbonation. This was tried with NaOH and with lime. Although the results, even with lime, were good on synthetic solutions, the precipitation required excessive reagent or gave a low-grade product on the actual solutions obtained from upgrading primary precipitates.

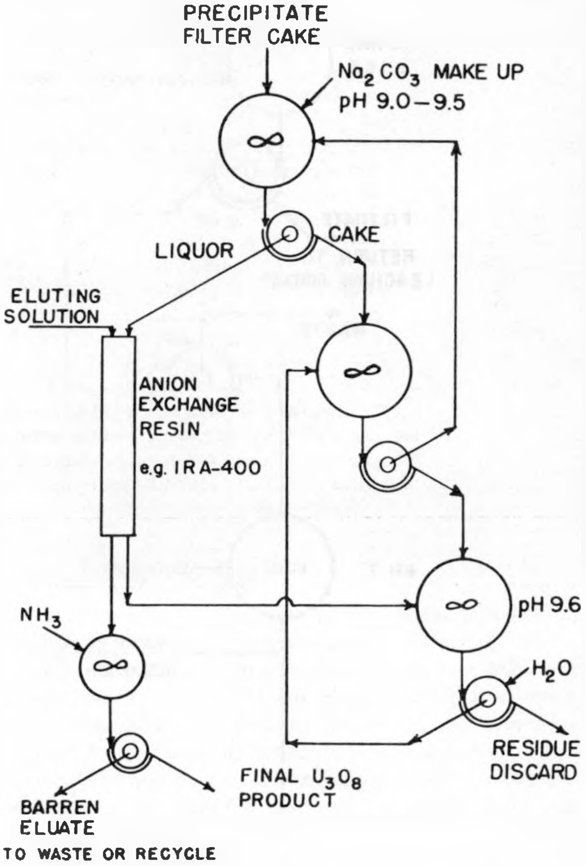


Fig. 2 — Carbonate upgrading process using anion-exchange for final purification.

It is believed that the uranium might also be removed by an ion-exchange step, although no tests with ion-exchange resins were made on carbonate solutions obtained from upgrading primary precipitates.

Rand primary precipitates obtained with dolomite can be leached countercurrently with 20 to 30 pounds of Na_2CO_3 per pound of U_3O_8 to extract over 95 per cent of the uranium if acid-leaching conditions are controlled to give a calcined-dolomite precipitate containing 5 per cent U_3O_8. A flow sheet for the process is given in Fig. 2. This flow sheet assumes that ion exchange will be used to recover the uranium from the carbonate solution. Metallurgical results of carbonate leaching of various types of Rand calcined-dolomite precipitates are given in Table 3.[9,11]

Lyometallurgical Upgrading

"Lyometallurgy" is a term coined by this laboratory to describe the use of leaching processes which do not use water as a solvent. The results of this method on many materials will be described in a subsequent issue of this journal.[12]

Table 3 — Carbonate Upgrading of Various Primary Precipitates

Primary precipitate*	Assay, % U_3O_8	Na_2CO_3 required, lb/lb U_3O_8	No. of leaches	Uranium extraction in carbonate pregnant liquor, %
Pulps neutralized to pH 3.5 before filtration	3.3	43.0	2	85.9
	4.9	17.5	2	89.1
	5.2	32.5	2	94.2
Extra MnO_2 added to primary leach liquor to oxidize all the iron; pulp neutralized to pH 3.5 before filtration	6.4	9.5	2	96.5
	5.6	20.5	2	92.2
	5.1	12.0	4†	96.0

*The primary precipitates used as feed were obtained from Blyvooruitzicht cyanide residues leached with H_2SO_4 and MnO_2, and the primary liquors were precipitated with calcined dolomite. If magnesia is used for precipitation, better products and better results are obtained, but magnesia of suitable grade is too expensive to use on Rand solutions.

†Countercurrent carbonate leach.

The lyometallurgical work done on Rand precipitate involved the use of ether and nitric acid. Several methods were tried. In the first method the precipitate was digested with nitric acid, dried, and leached with diethyl ether containing little or no nitric acid. This method was supplanted by a simpler one in which the precipitate was leached directly with ether containing nitric acid. The second method was more selective, required less nitric acid, and eliminated one operation as well as the need for recovering nitrates from the residue. Acid leaching of these precipitates in water gave unfilterable slurries, but the ether pulps filtered with no difficulty. The filtration rate with ether was several hundred times greater than with water.

Neutralization of the pregnant ether solution with ammonia gas precipitated uranium hydroxide and ammonium nitrate.

This mixed granular precipitate filters readily. The ether, after uranium precipitation, is available for reuse, and what remains with the residue and the uranium precipitate may be recovered by vacuum-flashing. The ammonium nitrate may be removed from the uranium precipitate with a water leach, and the concentrated nitrate solution may be treated with lime to evolve ammonia for reuse. The calcium nitrate solution may be decomposed thermally to give nitric oxides, which are made into nitric acid for reuse.

Tests indicate that recovery of ether will exceed 99 per cent and that recovery of the nitric acid and ammonia will exceed 90 per cent. On this basis it appears that the process is likely to be as economical as the other retreatment processes, but it requires special equipment and additional development work. The flow sheet for the process[13] is given in Fig. 3, and metallurgical results are summarized in Table 4.

SELECTIVE PRECIPITATION

Preliminary Precipitation

The first attempts at selective precipitation on Rand leach liquors involved differential neutralization. It was found that ferric iron could be precipitated[14] (probably as a basic ferric sulfate) by neutralization to pH 3.5 with a loss of only one or two per cent of the uranium in the iron-bearing discard. Further neutralization brought down ferrous iron, silica, and alumina along with the uranium. Ferrous iron could be oxidized by the addition of stoichiometric amounts of MnO_2 and acid so that almost all the iron in solution could be eliminated[15] at pH 3.5, but even in the absence of iron uranium precipitates were still of low grade because of alumina, silica, and gypsum.

Some high-grade precipitates were obtained by reducing leach liquors and precipitating uranous hydroxide by neutralization to pH 3.5, but the recovery of uranium was poor. On the reduced solutions iron did not precipitate below pH 6, and, when precipitation did occur, the precipitate was white ferrous hydroxide

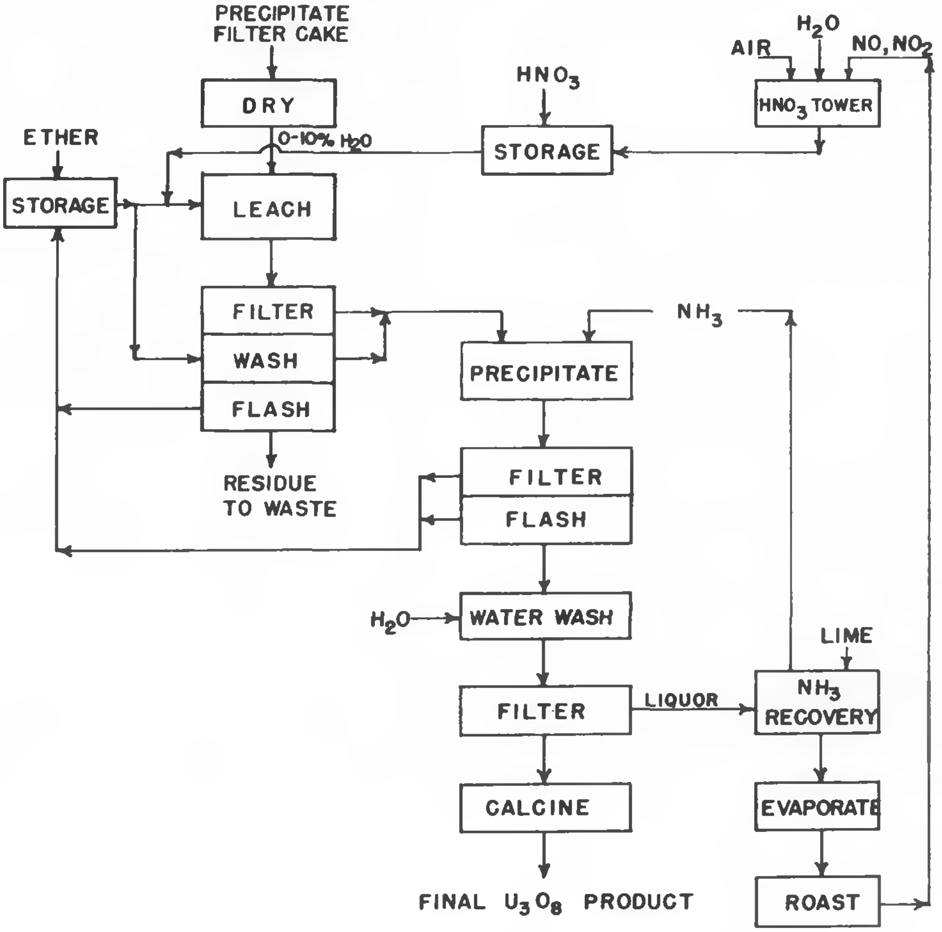


Fig. 3—Flow sheet for lyometallurgical upgrading.

Table 4—Typical Lyometallurgical Upgrading of Rand Precipitates

Precipitate	Assay, % U_3O_8	Leach time, min	U_3O_8 extracted,* %	Reagent consumption, lb/lb U_3O_8 extracted: Ether†	Reagent consumption, lb/lb U_3O_8 extracted: Nitric‡
A§	2.07	10	92.5	2.2	0.9
	2.32	20	96.2		
B¶	2.6	20	95.3	2.2	2.2

*The method used to evaluate the recovery involved analysis of the liquor for uranium. The grades of final products are therefore not available in the tests reported in this tabulation. Other tests have given final products assaying consistently above 90 per cent U_3O_8.

†Assuming 99 per cent recovery of solvent.

‡70 per cent HNO_3, assuming 90 per cent recovery of nitrate.

§Precipitate A obtained with calcined dolomite from partly neutralized Rand leach liquor, air-dried, leached with ether containing 5 per cent HNO_3 by volume, and washed with plain ether.

¶Precipitate B similar to A but digested with HNO_3 at 50 per cent solids, dried at 80°C, and leached with ether containing 2 per cent HNO_3.

714 076

DECLASSIFIED

rather than the green ferroso-ferric hydroxide which starts to precipitate at pH 5. Further neutralization beyond pH 3.5 gave complete recovery of uranium, but the precipitates were diluted with alumina and silica.[16] The final precipitates usually did not assay appreciably over 5 per cent U_3O_8.

Addition of orthophosphate was tried both with and without reduction of the uranium. Complete precipitation was obtained by neutralizing to pH 3.5. This precipitate also contains alumina and silica and (if not previously removed) ferric iron.[17] Addition of fluoride to reduced solutions was attempted, but, perhaps because of the silica present, the insoluble UF_4 did not precipitate when reasonable amounts of fluoride were used unless the solution was neutralized to pH 3.5, and then the results obtained were similar to those obtained with uranous hydroxide precipitation.[16]

Various organic reagents were tested as precipitants. Encouraging results were obtained only with long-chained amines. A large quantity of amine was required, although it could be recovered because uranium is leached from the amine with acid so that the amine can be returned for reuse. However, the slight solubility of these chemicals in the barren solution was sufficient to make the process uneconomical.[18]

Pyrophosphate Precipitation

As mentioned in the section on precipitate retreatment, it was found that pyrophosphate was a more selective precipitant for uranium than orthophosphate in the concentrated liquor derived from acid leaching of Rand precipitate. Pyrophosphate was then tried directly on reduced dilute leach liquors. It was found that addition of pyrophosphate in an amount equal to 1.5 to 2 times the stoichiometric amount needed for uranium would precipitate at least 90 per cent of the metal from reduced leach liquors containing as little as 0.1 g/liter of U_3O_8.

Pyrophosphate precipitation was tried on both the unneutralized leach liquor at pH 1.5 and on liquor which had been neutralized to pH 3.5. The unneutralized liquors still contained ferric iron and required much more reducing agent than neutralized liquors. However, the neutralized liquors consumed additional acid because the pH had to be lowered below 2 for reduction. Reduction commonly was accomplished with powdered iron, although other reducing agents and electrolytic reduction[19] could be used.

On the unneutralized liquors part of the uranium separated out on the iron during reduction. This phenomenon, termed "pseudocementation," was encouraged by a large iron surface and by the presence of minor quantities of orthophosphate derived from the ore. On liquor neutralized to pH 3.5 this phenomenon was not encountered, presumably because orthophosphate is removed with ferric iron before reduction.

Excellent results were obtained by pyrophosphate precipitation, using liquors neutralized to pH 3.5 before the filtration that precedes reduction. The amount of iron required for the reduction is about 1 pound per pound of U_3O_8. Ground cast iron can be used provided a sixfold excess is added. Excess iron can be recycled until completely consumed.

The uranous pyrophosphate precipitate is a turquoise-green gelatinous substance which flocculates and settles leaving a clear solution. The thickened precipitate is so fluffy that it contains less than 1 per cent solids. It can be further dewatered in a centrifuge to about 10 per cent solids.

As any phosphate is an undesirable compound in a refinery feed, its removal is necessary. This can be accomplished by digesting the centrifuge cake with solid sodium hydroxide (about 2 pounds per pound of U_3O_8). The uranium is converted to sodium uranate which can be filtered, washed, and ignited to give a product containing about 70 per cent U_3O_8 with about 1 per cent P_2O_5. Although the amount of pyrophosphate is small, it might be recovered from the sodium hydroxide leach for reuse. The flow sheet for this process is given in Fig. 4, and typical metallurgical results[20] obtained with partially neutralized leach liquors are given in Table 5.

A preliminary fundamental study has been made of the uranous phosphates. Uranium pyrophosphate precipitate is not crystalline unless heated to 600°C, and its composition is not constant. Uranous pyrophosphate is less soluble than uranous orthophosphate not only in pure solutions but also in leach liquors, provided the amount of alkali pyrophosphate added is not greater than twice the stoichiometric amount needed to form UP_2O_7. With an excess of pyrophosphate the uranium is complexed and precipitation is incomplete.[21] Tracer studies have shown that, if uranous sulfate is added to a solution containing a little pyrophosphate and up to twenty times as much orthophosphate, the pyrophosphate is completely and preferentially precipitated.

Excess pyrophosphate left in the barren solution is removed on the residue if this solution is recycled and the pyrophosphate does not build up.[22]

Pseudocementation Process

As mentioned before, it was found that uranium is removed during the reduction of simple leach liquors, and its removal is facilitated by a high surface on the iron and by the presence of phosphate. The Government Metallurgical Laboratory in South Africa has found that the presence of copper ions in solution is advantageous in that it allows the iron to be fully

714 077

DECLASSIFIED

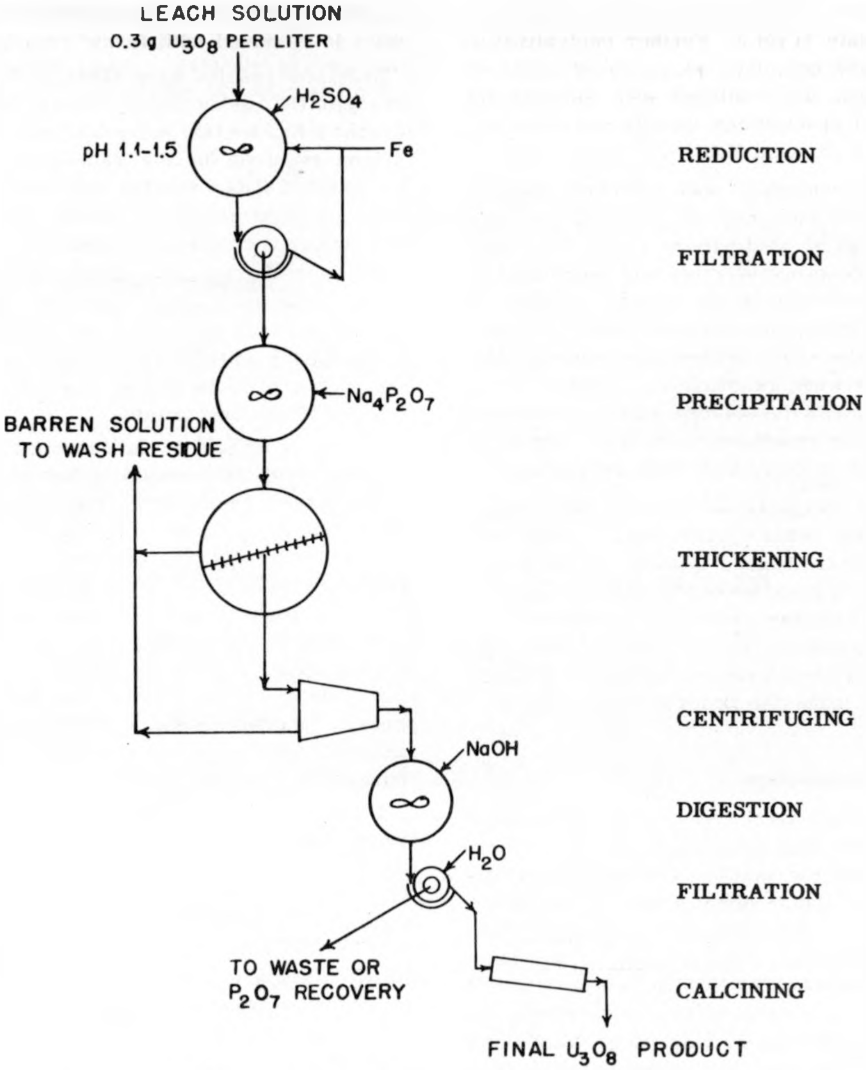


Fig. 4 — Selective precipitation process using pyrophosphate as precipitant.

Table 5 — Typical Results Obtained by Selective Precipitation Process Using Pyrophosphate as Precipitant[*]

Ore source	Product	Amount per kg of ore	U_3O_8 assay	Recovery, % of dissolved U
Western Reefs	U precipitate	0.258 g	47.2 %[†]	98.5[‡]
	Phosphate solution	5.0 ml	0.150 g/liter	0.3
Bylvooruitzicht	U precipitate	0.208 g	69.8 %	98.7[‡]

[*] In Western Reefs test the iron used for reduction was recirculated. In other tests the recovery figure assumes reuse of iron. Both results are from locked-batch cyclic tests.

[†] The excess iron is removed by settling and decantation, therefore uranium is contaminated with fine iron and carbon (ground cast iron used).

[‡] The balance of the dissolved uranium reports in the interstitial liquor discarded with the residue filter cake. It is a true soluble loss chargeable to this precipitation process.

711 078

DECLASSIFIED

consumed, gives good precipitation of the uranium, and gives a precipitate which can be easily handled. With or without copper, removal of uranium can be obtained by electrolytic reduction, and the uranium appears on the cathode, probably as an oxide or phosphate, mixed in the metallic deposit of iron or copper.

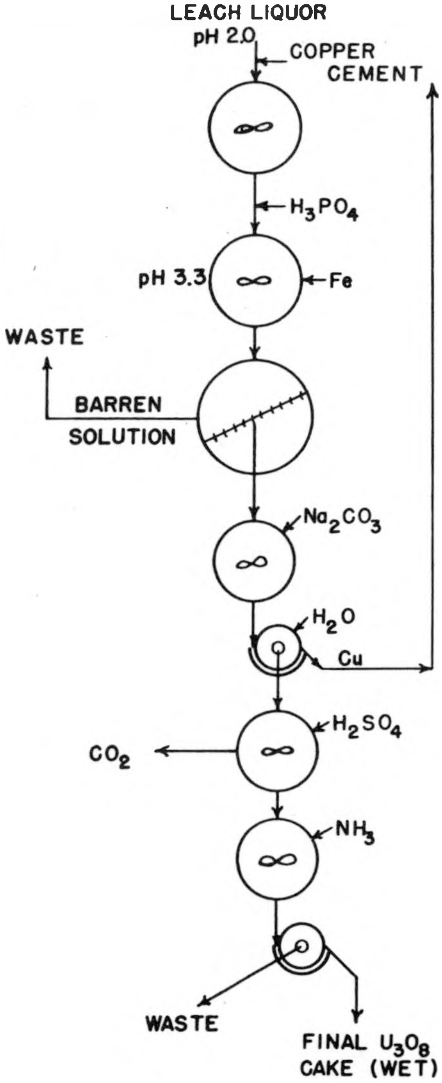


Fig. 5 — Pseudocementation process using copper and phosphate, as developed by the Government Metallurgical Laboratory of the Union of South Africa.

Uranium can be recovered by a carbonate leach of the iron-uranium phosphate or the copper-uranium phosphate precipitate or deposit, and a high-grade final product can be obtained from the carbonate solution.

It is assumed that the mechanism involved is a precipitation of uranous phosphate or hydroxide in the thin layer of electrolyte which assumes a relatively high pH because of dissolution of iron or directly by electrolysis. Precipitation is selective for uranium providing the pH does not rise too high.[23] The flow sheet used in the 1-ton-per-hour pilot plant in South Africa is given in Fig. 5.

Full reports on metallurgical results are not yet available, but the process has removed up to 95 per cent of the uranium using 4 to 5 pounds of ground cast

DECLASSIFIED

iron and 1 to 2 pounds of phosphoric acid per pound of uranium recovered. Consumption of other reagents is not known except that the copper has been recycled for periods of over one month without any addition. The trace of copper present in the leach liquors provides sufficient make-up.

A preliminary test on a leach solution of copper uranium ore from Hite, Utah, gave promising results. Addition of slightly over the stoichiometric amount of phosphate resulted in the precipitation of over 90 per cent of the uranium and all the copper when the solution was agitated with powdered iron. The uranium was leached from the precipitate with carbonate.

ADSORPTION

Preliminary Experiments

Some experiments were run in an attempt to remove uranium from leach liquors by adsorption on activated charcoal. Uranium removal in these experiments was slight unless the solution was neutralized to pH 3.5, where uranium is almost ready to start precipitating. Under these conditions uranium was removed by the carbon but alumina, silica, and ferrous iron were also removed. The carbon could be regenerated by leaching in strong acid, but precipitation of this acid solution gave a low-grade product. The removal of uranium with a long-chain amine, mentioned in the section on selective precipitation, may also have involved some form of adsorption.

Experiments were also run with cation-exchange resins. The cation resins adsorb uranium completely from leach liquors, but they also pick up the iron, aluminum, calcium, and magnesium. Only the silica and water were rejected. Accordingly, the degree of purification obtained was less than that obtained by simple neutralization. No useful degree of selectivity between the various metals was shown by the resins, but removal of water and silica might be useful if uranium could be easily precipitated selectively or solvent-extracted from the concentrated eluate. However, the few experiments which were run showed no appreciable advantage.[24]

Anion Exchange

Uranium forms complex ions with many organic and inorganic acids. Experiments at other laboratories have shown that the new strong-base anion-exchange resins have a high affinity for complex anions and that uranium can be adsorbed from sulfuric, hydrochloric, and phosphoric acid solutions.[25] Our experiments have shown that uranium is selectively adsorbed from sulfuric acid leach liquors of each ore tested.

Various anion-exchange resins have been tested in these solutions, and Amberlite IRA-400, a strong-base bead-form exchanger, manufactured by Rohm & Haas Co., was found to be best. With a single resin column the leach liquor is passed through the resin until some uranium appears in the effluent. Alternately, several resin columns can be used in series and the solution passed through until uranium appears in the effluent of the last column. By this time the resin on the first column is saturated, that is, it is unable to adsorb any more uranium.

Uranium is then eluted from the resin with a chloride or nitrate solution, approximately 1M, which contains 0.1M of acid to prevent precipitation of the uranium and ferric iron in the column. Uranium can then be precipitated from the eluate with ammonia. The resulting precipitate filters well and does not have to be washed because the ammonia salts in this product are removed by heating. The barren eluate can be reused, but chloride or nitrate must be added in an amount equal to that adsorbed by the resin during elution. Normally this represents about 10 per cent of the total and is made up by the addition of acid which not only restores the chloride or nitrate concentrations but gives the eluate the proper acidity for reuse. The amount of eluting solution needed per unit of resin is constant regardless of how much uranium is on the resin.

The choice between the use of a single and a multiple column depends on many factors. The use of multiple columns requires less resin and small amounts of eluting reagents, gives a purer product, but requires more equipment and more labor. The flow sheet for the general process is given in Fig. 6, assuming, for simplicity, that a single column is used.

By limiting the flow rate and the amount of solution treated per unit of resin, it is possible to make uranium recovery 100 per cent complete on all leach solutions. For commercial operation some loss will be accepted in the interest of production. This loss, however, need not be as much as 1 per cent.

Locked-batch cyclic tests have been run using the flow sheet shown. In these tests a minimum amount of resin was used in order to emphasize any difficulties that might be encountered from recycling barren and eluting solutions. With this procedure losses of several per cent were sometimes obtained. Table 6 summarizes the results obtained on Rand ores using one, two, or three columns in series, simple leach liquors or partly neutralized leach liquors, and thickeners or filters for dewatering. The results obtained with three domestic ores are also given. Other laboratories have used anion-exchange resin to recover uranium from sulfate leach liquors of shales,[26] carnotites,[27] and Canadian pitchblende ores[28] from carbonate leach liquors[29] and from phosphoric acid.[30]

DECLASSIFIED

Under proper conditions the precipitate assays over 50 per cent U_3O_8 with iron as the principal impurity. On richer solutions and solutions low in iron, precipitate grades of 90 per cent U_3O_8 are frequently obtained.[31] IRA-400 resin has been tested in Rand solutions through 500 cycles without substantial loss in capacity. Estimates indicate that the ion-exchange process will recover uranium from Rand solutions at about half the cost of the other methods.

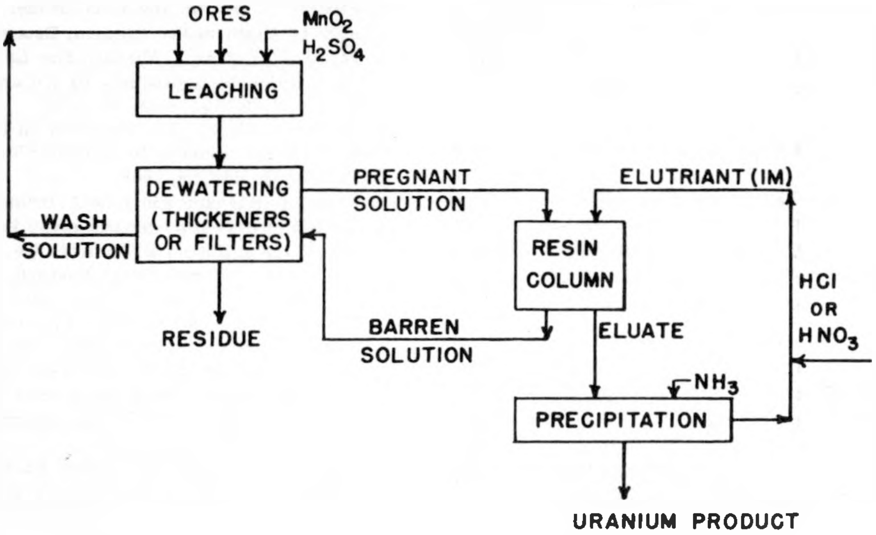


Fig. 6—Flow sheet for uranium recovery with anion-exchange resins.

Table 6—Summary of Results from Locked-batch Cyclic Tests Using Ion-exchange Resin

Ore	Assay % U_3O_8	Dilution ratio of solution to ore	pH	No. of columns	U_3O_8 recovery, % Dissolved*	U_3O_8 recovery, % Total	Resin, cu ft/ton/day
Rand 396-63	0.025	2.00	1.3	1	93.0	79.0	0.242
	0.025	0.50	1.2	1	97.9	77.6	0.184
	0.026	0.663	1.2	2	96.0	76.1	0.104
	0.025	0.663	1.2	3	94.0	74.3	0.095
	0.025	0.50	3.4	1	90.1	70.8	0.115
Marysvale, Utah, Q3	0.20	1.6	0.9	1	98.8	90.0	0.96
White Canyon, Utah, R-4	0.32	1.0	1.2†	1	91.5	85.0	0.95
Sunshine, Idaho, K2+5	0.46	0.8	0.9	1	99.2	89.1	2.31

*Unrecovered uranium due to poor washing and/or overloading columns.
†Original pH 0.7; pH adjusted with limestone.

From our empirical tests of the method on various leach liquors some idea has been obtained of the factors affecting the selective adsorption of uranium on ion-exchange resins. The main ions adsorbed have been sulfate, bisulfate, and the complex sulfate anions of uranium and iron. Of these the uranium complex is most tightly held. The amounts of these ions adsorbed at equilibrium depend on the concentration of each ion. The concentration of the uranium and iron complex ions depends on additional factors including pH. In plant operation, of course, nonequilibrium conditions are used, and here the flow rate and temperature are factors. To understand the reactions involved

714 C81
DECLASSIFIED

and the quantitative effects of the different variables requires a considerable amount of further research. A few such investigations are now under way. These matters may be dealt with in a future article.

Nevertheless the results with ion exchange are so promising that pilot plants are now in operation on the Rand and full-scale plants are being designed. It is also likely that new plants to treat domestic materials will include the ion-exchange step.

Use of Ion-exchange Resins in the Ore Pulp

Although ion exchange does offer a general method of recovering uranium from ore leach solutions, there are some ores which contain slimes whose quantity or quality makes separation of a leach solution from the residue difficult or even impractical.

Consideration has been given to the use of resins in the pulp to pick up the dissolved uranium so that thickening or filtering will not be needed. Preliminary experiments have shown that the resin does work in a pulp, but separation of normal bead-form resin is difficult, and confining the resin in porous containers slows the reaction. Pieces of resin in sheet form which are easily separated from the pulp have been obtained from Rohm and Haas. Promising results were obtained.[32] Considerable development work remains to be done before this process can be applied in a plant. When our work on the use of resins in the pulp is nearer completion, we may be able to present it in this journal.

SUMMARY

For ores that can be dewatered ion exchange presents a general, flexible, economical method of recovering uranium from dilute impure leach liquors into a high-grade product suitable for refinery feed. Several other practical recovery processes have been developed. While they are less economic than ion exchange for treating Rand solutions, they should be considered in comparison with ion exchange for new problems.

REFERENCES

1. A. M. Gaudin et al., The Recovery of Uranium from Low-grade Ores, J. Met. Ceram. 5: 38, June 1950.
2. Charles S. Abrams, Single-stage Leach (III), Report MITG-A91, July 1, 1950.
3. John J. Brunner, Robert L. Barnard, and Sara E. Bailey, Acid Leaching of Low-grade Uranium Precipitates from Rand Ores, Report MITG-A76, Oct. 28, 1949.
4. T. V. Arden and Elizabeth Napier, Preliminary Investigations on a Method for the Concentration of Uranium from Rand Ores, Report CRL-AE-34, May 1949.
5. Sara E. Bailey, Retreatment of Low-grade Hydroxide Precipitates by the Phosphate Process, Report MITG-A-77, Mar. 3, 1950.
6. Gilman Y. Murray and John Dasher, Carbonate Treatment of Uranium Precipitates, Report MITG-A49, June 21, 1948; Eugene J. Michal, The Leaching of Uranium from Insoluble Hydroxides by a Carbonate Treatment, Report MITG-A51, Sept. 30, 1948.
7. Eugene J. Michal, The Recovery of Uranium from Low-grade Leach Liquors by Selective Precipitation, Report MITG-A53, Nov. 24, 1948.
8. Robert L. Barnard and John J. Brunner, Carbonate Extraction of Uranium from Dissolved Low-grade Hydroxide Precipitates, Report MITG-A73, Apr. 3, 1950.
9. Charles S. Abrams, David Kaufman, and John Dasher, Extraction of Uranium from Rand Precipitates with Carbonates (I), Report MITG-A72, June 24, 1949.
10. John J. Brunner, Acid Digestion—Peroxide Retreatment Process, Report MITG-A78, Jan. 6, 1950, and Single-stage Leaching of Some Rand Ores with Reagents Produced by the SO_2-Air Process, Report MITG-A92, July 1, 1950.
11. Charles S. Abrams and David Kaufman, Extraction of Uranium from Rand Precipitates with Carbonates (II), Report MITG-A81, Feb. 7, 1950, and Extraction of Uranium from Rand Precipitates with Carbonates (III), Report MITG-A86, July 1, 1950.
12. A. M. Gaudin, John Dasher, David Kaufman, F. W. Bloecher, Jr., and Paul Galvanek, Jr., Lyometallurgy, A New Method of Extracting Uranium from Its Ores, Report MITG-260.
13. Paul Galvanek, Jr., and David Kaufman, Application of the Solvent Leaching Process for the Concentration of Uranium from Rand Ores, Report MITG-A79, Nov. 15, 1949, and Further Studies on Solvent Leaching Uranium Recovery from Eldorado Concentrate, Congo Precipitate, Rand Precipitate, and Carnotites, Report MITG-225, Mar. 20, 1950.
14. John J. Brunner, Differential Precipitation of Uranium from Iron by Neutralization, Report MITG-A38, June 21, 1948.
15. John J. Brunner, Further Studies on the Double Precipitation Process, Report MITG-A74, Aug. 5, 1949.
16. Robert L. Barnard, Neutralization of Reduced Rand Leach Solutions, Report MITG-A75, Dec. 16, 1949.
17. Sara E. Bailey, Phosphate Precipitation of Uranium from Rand Ore Leach Solutions and Retreatment of the Phosphate Precipitates, Report MITG-A62, June 1, 1949; Elizabeth Napier and D. Pearson, Investigations on the Preparation of a High-grade Uranium Concentrate from Acid Leach Liquors Derived from Rand Ore Cyanide Residues, Report CRL-AE-50, February 1950.
18. Sara E. Bailey, Precipitation of Uranium by Organic Compounds, Report MITG-A52, Dec. 31, 1948.
19. Wilfred Freyberger, Electrolytic Reduction of Uranyl and Ferric Sulfate Solutions, Report MITG-A95, May 12, 1950.
20. Sara E. Bailey, The Selective Precipitation of Uranium from Reduced Rand Ore Leach Solutions with Tetrasodium Pyrophosphate, Report MITG-A85, Mar. 20, 1950; John J. Brunner, Single-stage Leaching of Some Rand

DECLASSIFIED

Ores with Reagents Produced by the SO_2-Air Process, Report MITG-A92, July 1, 1950.

21. James H. Pannell and Emelia M. Rubino, Some Properties of Uranous Phosphates, Report MITG-245, Sept. 15, 1950.
22. James H. Pannell and John J. Brunner, Tracer Studies of the Pyrophosphate Process, Report MITG-A99, Sept. 14, 1950.
23. Sara E. Bailey, Pseudocementation Interference with Phosphate Precipitation of Single-leach Process X Liquors, Report MITG-A90, July 1, 1950; John J. Brunner, Simultaneous Precipitation of Uranium and Copper, Report MITG-A103, Oct. 31, 1950; Galen W. Clevenger, Electrolytic Deposition of Uranium from Acid Leach Solution, Report MITG-A106; R. R. Porter and J. K. E. Douglas, Operations of the Blyvooruitzicht Pilot Plant for the Period Dec. 22, 1949, to Feb. 26, 1950, G.M.L. Progress Report 23, Leaching, and Operation of the Blyvooruitzicht Pilot Plant for the Month of March 1950, G.M.L. Progress Report 24, Leaching; R. R. Porter and J. C. Geentema, The Precipitation of Uranium on Detinned Scrap Iron, G.M.L. Progress Report 25, Leaching, October 1949; R. R. Porter and E. T. Pinkney, Operations of the Western Reefs Pilot Plant for the Period from Mar. 28 to May 12, 1950, G.M.L. Progress Report 26, Leaching, and Uranium from Solutions Derived from Rand Ores, G.M.L. Progress Report 28, Leaching, June 1950.
24. Norman Schiff, Experiments on Rand Leach Liquors with Cation-exchange Resins, Report MITG-A64, Aug. 1, 1949.
25. K. A. Kraus and R. E. Moore, Separation of Thorium, Protactinium, and Uranium with Anion-exchange Columns in HCl Solutions, Report ORNL-330, Apr. 27, 1949, Anion-exchange Studies. I. Separation of Zirconium and Niobium in HCl-HF Mixtures, Report ORNL-661, May 25, 1950, Anion-exchange Studies. II. Tantalum in Some HF-HCl Mixtures, Report ORNL-662, Apr. 26, 1950; A. E. Bearse et al., Progress Report for Month of December 1948, Report BMI-JDS-158, Dec. 30, 1948.
26. R. A. Ewing, G. A. Lutz, and A. E. Bearse, Final Report on Recovery of Uranium from Shales, Report BMI-JDS-210, Sept. 30, 1949.
27. R. H. Bailes, Dow 31 Progress Report for June 1950.
28. R. H. Bailes, Dow 37 Progress Report for December 1950.
29. E. J. Kahler et al., Precipitant Studies, Final Report BMI-JDS-211, September 1949; R. H. Bailes, Dow 28 Progress Report for April 1950.
30. R. H. Bailes, Recovery of Uranium from Phosphate by Ion Exchange, Dow Summary Status Report 3, Dec. 7, 1949.
31. Norman N. Schiff, Removal of Uranium from Rand Leach Liquors with Anion-exchange Resins, Report MITG-A93, July 1, 1950; Sara E. Bailey, Removal of Uranium from Rand Leach Liquors with Anion-exchange Resins. II. Tests with Process X Leach Liquors, Report MITG-A96, July 1, 1950; Robert L. Barnard, A Preliminary Study of the Adsorption of Uranium(VI) and Other Metallic Ions by Anion-exchange Resins, Report MITG-A97, Aug. 18, 1950; Norman N. Schiff, Removal of Uranium from Rand Leach Liquors with Anion-exchange Resins. III. Cyclic Tests with X and Y Process Leach Liquors Obtained by Filtration, Report MITG-A102; D'Arcy George, Edmund G. Brown, and Richard Kennedy, Mineral Engineering Report on Marysvale Ores, Q-1, Q-2, and Q-3, Report MITG-253; Robert Woody, D'Arcy George, and Charles S. Abrams, Recovery of Uranium and Silver from the Uranium Ore Samples from the Sunshine Mine, Kellogg, Idaho, Report MITG-258; D'Arcy George, Charles S. Abrams, Paul Galvanek, and F. W. Bloecher, Jr., Preliminary Mineral Engineering Studies on Copper-Uranium Ores, R-1 and R-2, Report MITG-263.
263.
32. Fred Oberg and Robert D. Macdonald, Preliminary Tests on Resin-in-the-Pulp Process, Report MITG-A101.
33. Sara E. Bailey, The Precipitation of Uranium by Inorganic Acids of Groups V and VI, Report MITG-A44, Mar. 31, 1948.

January 1951

714 083

Survey of Processes for Separation of the Products of Nuclear Reactors

By J. H. Arnold, M. Benedict, J. A. Finneran, S. Golden,
and F. B. Grosselfinger

Hydrocarbon Research, Inc., New York

and H. M. Elsey

Westinghouse Electric Corporation, Pittsburgh

Report TID-458 (Del.)

ABSTRACT

The primary objective of the subject survey has been the evaluation of separation processes, for future installations, for recovering and decontaminating plutonium and uranium from irradiated natural uranium and concentrating the residual radioactive waste. In addition, processes have been considered for treating enriched uranium and for handling the cores and blankets of plutonium and U^{233} breeders. Processes are evaluated from the standpoints of efficiency of recovery and decontamination of plutonium and uranium, concentration of fission products, probability of success on a production scale, capital cost, operating cost, and hazard.

INTRODUCTION

In accordance with the provisions of Contract AT-(30-1)-697,[*] Hydrocarbon Research, Inc., has made a survey of processes for separating the principal products of the irradiation of uranium and thorium by neutrons.

Instructions from the Atomic Energy Commission have made the primary objective of this survey the evaluation of separation processes for recovering and decontaminating plutonium and uranium from irradiated natural uranium and concentrating the residual radioactive waste. The survey has been concerned with the intrinsic merits of separation processes for new installations rather than with the possible modification of existing facilities at Hanford.

When the survey was started, no new separation plants were immediately in prospect, and the primary

---

[*] Editors' Note: In early June of 1949 Hydrocarbon Research, Inc. was requested by the Division of Research to undertake a survey of chemical processing problems associated with the operation of nuclear reactors. The contract, negotiated and administered by the New York Operations Office, extended from June 1949 to early July 1950. The scope of the contract is stated, in part: "The Contractor ... shall undertake engineering studies and evaluations of processes for separation of the principal substances remaining after irradiation of fissionable and source materials by neutrons in a nuclear reactor ... . The surveys will not be restricted by precedent but will evaluate processes in terms of inherent merit. Process evaluation will include consideration of the efficiency of recovery and decontamination of fissionable and source material, the degree of concentration of fission-product residue, the probability of successful operation on a production scale, estimated capital and operating cost, potential hazard, and waste-disposal difficulties ... . Although the primary emphasis will be on processes in which the starting material is irradiated natural-uranium metal, the studies may also consider processes in which the feed material is enriched uranium or uranium in compounds or alloys ... ." The final report was dated July 12, 1950 and, after minor revisions, appears as this article.

714 C84

DECLASSIFIED

utility of the survey was expected to be the guidance it would offer in formulating programs for research and development on separation processes. But while the survey was in progress, the construction of new reactors and a new separation plant away from Hanford became imminent, so that this survey has an immediate applicability over and above the initial expectation. It is hoped that the conclusions of this report will be helpful in selecting the process to be used in this new separation plant.

In addition to this primary objective the survey has also considered processes for treating enriched uranium and for handling the core and blanket of plutonium and U^{233} breeders.

The results of the survey are presented in this report. To the extent of available information, processes are evaluated from the standpoints of efficiency of recovery and decontamination of plutonium and uranium, degree of concentration of fission-product residue, probability of successful operation on a production scale, capital cost, operating cost, and hazard. Detailed descriptions and flow sheets are not included since this information is adequately presented and readily available in the AEC literature.

The production of fissionable materials consists broadly in three operations: (1) preparation of the fuel elements, (2) nuclear conversion of the fuel in the reactor, and (3) separation and decontamination of the reactor products. Reactor engineering thus has an important influence on the nature and magnitude of the associated separation processes, and it must be considered in a proper evaluation of separation processes. For example, the Hanford reactors require the many costly operations of forming fuel rods, canning slugs, irradiating the slugs, dissolving the irradiated slugs, recovering and decontaminating plutonium, recovering and decontaminating uranium, and, if the latter is returned to the reactor after enrichment, converting the uranium to metallic form.

The high cost of the chemical and metallurgical operations at Hanford is typical of most of the nuclear-conversion processes now visualized by the AEC. Similar high costs are anticipated, for example, in reprocessing the fuel elements of an enriched reactor or in extracting bred material from a breeding blanket and reworking the source material of the blanket. These high costs are largely a consequence of the present practices of (1) recycling the source or fissionable material many times through a reactor before it is completely used up, (2) completely reprocessing unconverted as well as converted material, and (3) the need for extensive metallurgical operations and fabrication of intricate reactor parts. In this connection the various nuclear-conversion processes now under consideration by the AEC have been examined to see if one or more of these practices can be dispensed with in order that the cost added to the products of nuclear conversions by chemical and metallurgical operations may be reduced.

Also adding to the cost of the separation processes are the inherently difficult separations required, the essential high purity of the recovered materials (plutonium and uranium in the case of the plutonium-production reactor), the high degree of recovery demanded by the value of the materials being recovered, the hazards involved in handling radioactive materials (which necessitate many operations by remote control), and the hazards and expense of storing large volumes of radioactive wastes.

It is thus obvious that any separation and recovery process, whether it be precipitation, solvent extraction, fluorination plus distillation, liquid metallurgy, etc., will be costly. Hence any simplification or reduction of the separation and recovery required, by modification of reactor design, e.g., nature of fuel element, neutron economy, and yield of plutonium, can possibly lead to larger savings than selection between different separation processes once the reactor design is set. An over-all development program integrating reactor design and separation processes would almost certainly lead to simplification of the separation processes and, possibly, of the reactor design.

The more important conclusions and recommendations for full-scale application and further development of the various processes studied, based upon the present state of the art, are presented in the following section. A comparison in some detail of the various processes for the simultaneous separation and recovery of plutonium and uranium is found in the section on separation processes for reactor products. This section also compares processes for recovering uranium from stored waste at Hanford. A discussion of those processes still in the early stages of development which offer promise of surpassing presently contemplated processes in certain applications is found in the section on development of new separation processes. The relation of reactor engineering to the type of processes needed for separating reactor products is discussed in the section on joint development of reactors and separation processes.

RECOMMENDATIONS AND PRINCIPAL CONCLUSIONS

Joint Development of Reactors and Recovery Processes

Prior to the successful operation of the first Hanford reactor it was sound judgment to design a reactor which appeared to have the highest probability of success and to accept the separation and recovery problems which such a design entailed. However, now that considerable experience has been acquired in the operation of the Hanford production reactors and the various experimental reactors, the time has come to examine integrated reactor designs, whether for the production of fissionable materials or for power, which balance the economics and dependability of all operations. Particular emphasis is directed to the need for integrated design of breeder reactors. It now seems probable that very high recoveries of fissionable material will be required at least in the initial low–burn-up reactors and that such high recoveries will be realized only with great effort. Thus it is conceivable that the entire success of the initial breeder reactor may depend upon the selection of a type of fuel which will minimize the separation and recovery problem. Direct collaboration between reactor development and recovery-process development is not in evidence at the present time to the extent required to produce integrated designs.

It is therefore strongly recommended that present liaison between these two fields be replaced by close coordination so that the problems confronting the group designing the reactor and the problems confronting the group developing recovery processes will receive mutual consideration. This necessarily requires that both groups be part of a single, closely knit organization. Such joint development will result in better over-all processes at lower cost.

Precipitation Processes

In the present state of the art none of the precipitation processes tried or suggested appears to merit further consideration nor does there now appear to be any justification for spending further time or money in the development of new processes of this type.

Solvent Extraction Processes

The Purex process is by far the best of the solvent extraction processes which have been developed. Its principal advantages are effectiveness of decontamination, low cost of solvent, use of volatile and easily recoverable salting agent, and compact packaging of fission-product waste.

The Purex solvent, tributyl phosphate, appears to be a generally suitable solvent in other extraction applications such as those of a breeder reactor, the decontamination of enriched-uranium fuel elements, and the separation of U^{233} from irradiated thorium.

The Purex process is yet to be demonstrated in a reasonably sized pilot plant. It is strongly recommended that such a demonstration, which has been scheduled, be made without delay.

The Purex process is not the perfect solvent extraction process, but it is the end result of a large amount of work by a number of different investigations, and it appears almost certain that the point of diminishing returns has been reached in the development of this type of process. Therefore, unless preliminary estimates indicate a worth-while improvement over the present Purex process, further work on the development of new solvent extraction processes or new solvents is not recommended.

Fluorination Processes

Of the separation processes which have not been thoroughly studied experimentally, the class of processes which convert the reactor products to fluorides, which are subsequently separated by distillation, seems most promising for further investigation. Sufficient additional experimental work, on the laboratory scale, should be carried out to provide the basic physical data needed to evaluate these processes. This work would include a determination of the physical properties of fluorides of plutonium and fission products and interhalogen compounds and phase-equilibrium studies on mixtures of these substances with each other and with UF_6. The corrosion rate of materials of construction for handling these materials and fluorine under the conditions of the process should be determined. We understand that such laboratory work is in progress.

When sufficient basic data have been secured, a preliminary engineering design and an economic analysis of a separation plant using this type of process should be made to establish the approximate economics of the process relative to the Purex process.

If the process continues to look promising after such a preliminary study and if full-scale application appears attractive, pilot-plant investigation of the process would be indicated.

Liquid-metal Processes

Liquid-metal processes have been suggested on the basis of certain calculations, and a few small-scale experiments have been made. However, no such process has yet been demonstrated even on a laboratory scale.

A successful liquid-metal process would result in a large reduction in the size of equipment and in the elimination of a large number of chemical-conversion steps which are required in present processes since the uranium would be processed entirely as a metal. Such a process would be particularly advantageous when applied to a plutonium reactor using fortified or enriched uranium as fuel. Then the recovered uranium could be used directly as the metal. Less advantage would result for applications to plutonium reactors using only natural uranium as fuel for then it would probably be desirable to convert the recovered metallic uranium to the hexafluoride for processing in the diffusion plant.

It is recommended that limited development work be conducted on a liquid-metal process for handling slugs from a plutonium-production reactor. However,

DECLASSIFIED

no large expenditure of time or money should be made until an application for such a process exists and until available data indicate that such a process can compete with other known processes.

Separation Processes for Breeder Reactors

Since breeding is primarily a process for making nuclear power available in increasing quantities, the economic aspects of the development of breeders and their associated separation plants are of paramount importance. In view of the extremely costly development program which is involved before a breeder reactor can be built to compete with a conventional power plant, we believe that present emphasis should be placed primarily on (1) securing the basic physical data needed to set the conditions under which breeders and their recovery plants might be operated and (2) carrying out preliminary engineering designs of a breeder reactor from which an estimate of the cost of power produced in such a reactor could be made.

Suggestions have been made of the directions to be followed in reducing the cost of the recovery plant associated with a breeder:

1. The fraction of fissionable material burned up per pass through the core should be made as high as possible.
2. In a breeder whose main objective is to produce power economically rather than to achieve a high net rate of production of fissionable material, the maximum amount possible of breeding should be done in the core in order to minimize the rate of separation processing.
3. Production of power in a thorium-U^{233} breeder seems to have potentialities of simplified chemical processing which have not been fully appreciated. There is a good prospect of achieving a high rate of breeding in the core, and the separation of U^{233} from thorium can be effected by taking advantage of the difference in volatility between UF_6 and ThF_4.
4. The process under development at Brookhaven which seeks to extract U^{233} continuously, in the form of UF_6, from the ThF_4 blanket of a reactor would be an attractive feature of a U^{233} breeder. The laboratory program to secure the basic data on reaction rates needed to set the operating conditions for such a process should be completed. Investigation of the process on a larger scale should await favorable engineering appraisal of the economics of producing power in a thorium-U^{233} breeder.

SEPARATION PROCESSES FOR REACTOR PRODUCTS

The production of fissionable materials by nuclear reactions is conducted in two distinct phases: (1) actual production in the nuclear reactor and (2) separation of the fissionable material from the source material in which it is formed. This report is concerned primarily with the latter phase, and in the following paragraphs consideration will be given to each of the many processes which have been proposed to effect the desired separations. The various processes are, in general, well known and have been fully described elsewhere; hence in the interest of brevity, no effort is made herein to provide descriptions of the processes. Rather, an effort will be made to appraise each process in terms of its relative merits.

Precipitation Processes

Bismuth Phosphate Process. The bismuth phosphate precipitation process has long been used at Hanford to effect the separation of plutonium from uranium and fission products. This process, utilizing the phenomenon of coprecipitation, was chosen largely because the early work on plutonium chemistry, confined to minute amounts of the element, made great use of precipitation reactions, a familiar technique in the field of radiochemistry. At the present time the principal consideration behind the choice of a precipitation process has disappeared since the physical and chemical properties of plutonium in bulk are now well known.

The great disadvantage of the bismuth phosphate process is that it does not recover the unconsumed uranium, and as a result additional equipment is now urgently needed at Hanford to recover uranium from stored wastes as well as from current production.

Other disadvantages of the bismuth phosphate process are as follows:

1. The waste volumes from the process are large, requiring extensive and expanding storage facilities. Such large waste volumes are to be expected from precipitation processes which require the handling of large amounts of material containing the desired product in low concentrations.
2. While the plutonium losses of this process are not very great (about 2 to 3 per cent in current production), the losses are not so low as to be negligible.
3. The waste solutions from the bismuth phosphate process contain so much material other than uranium and fission products that the recovery of uranium from these solutions is made additionally complicated.
4. The operating cost is high owing to the high raw-material and high waste-disposal costs and partly owing to relatively high labor costs.

Uranyl Ammonium Phosphate Process. The uranyl ammonium phosphate process (UAP) has been proposed to effect the recovery and decontamination of uranium from Hanford waste. Although there is little doubt that this process can achieve the intended separation, it is not so attractive as solvent extraction for this purpose.

Several disadvantages of the UAP process may be noted as follows:

1. The decontamination of uranium is poor.

2. The process is more costly with regard to both capital cost and operating cost.

3. The process is inflexible as regards feed compositions. The ionic composition of the feed must be closely controlled, and it seems unlikely that the process could be rapidly adapted to accommodate waste material from current plutonium production.

4. The waste volumes are approximately 20 per cent greater than presently produced by the bismuth phosphate process.

Electrochemical Precipitation Process. The electrochemical precipitation process, like the UAP process, is intended to effect the recovery and decontamination of uranium stored underground. While insufficient development work has been done to date to permit an evaluation of its operating performance, this process has one significant advantage over other precipitation processes in that it does not require the use of large amounts of precipitation agents. This feature would reduce significantly the chemicals costs for such a process and reduce the dilution of fission products by other solids. Nevertheless it seems unlikely that an electrochemical process can be developed which will be able to compete with solvent extraction.

Solvent Extraction Processes

General. Solvent extraction was first considered in 1943 as one of several alternatives for effecting the plutonium-isolation step at Hanford. Although not adopted for installation, the successful operation of a pilot plant indicated the feasibility of utilizing solvent extraction to effect the entire chemical-separation operation. At that time the process offered many advantages over the bismuth phosphate process, and a development program was initiated. During the past few years the program has been greatly expanded.

Redox Process. The Redox process was the first practical solvent extraction process to be developed. It has been amply demonstrated in the pilot plant, and it showed, for the first time, the following advantages over its predecessor, the bismuth phosphate process:

1. Process materials are essentially all liquid, and material handling is simple and compact.

2. In general, the corrosiveness of the solutions encountered is not severe.

3. The equipment used is of a conventional and reliable type and can reasonably be expected to operate for long periods of time without mechanical failure.

The following are disadvantages of the process:

1. The solvent used, hexone, has a low flash point.

2. The raw-material cost, particularly that of aluminum nitrate, is high. The cost of the chemicals varies from \$1000 to \$2000 per ton of uranium, depending upon the number of cycles employed.

3. The waste volume is quite high, 2960 gal/ton of uranium for a 2-cycle uranium process.

Purex Process. The recently developed Purex solvent extraction process has the following advantages over the Redox process:

1. The use of a volatile salting agent, e.g., nitric acid, makes the recovery of this material quite simple, thereby reducing raw-material cost.

2. The waste volumes can be markedly reduced by simple evaporation.

3. Raw-material costs are low, e.g., nitric acid, 2.5 cents per lb (\$1.58/lb-mole) as compared with aluminum nitrate, 12.0 cents per lb (\$45.00/lb-mole).

Very minor disadvantages of the Purex process compared to the Redox process are as follows:

1. The acidity is higher, about 5N, thus possibly aggravating corrosion.

2. Larger columns are required for the same uranium throughput.

Butex Process. Insufficient information was obtained on the Butex process, developed by the Canadians at Chalk River and the British at Harwell, to make a firm comparison with the Redox and Purex processes. It is very similar to the Purex process, using dibutyl carbitol as the solvent in place of tributyl phosphate. On the basis of limited information it appears to be superior to the Redox process but slightly less attractive than the Purex process. The reported completeness of decontamination of plutonium is less than the observed decontamination with Purex, so more cycles may be required to effect the same degree of decontamination as Purex. Also at last report the Canadians were experiencing difficulty in separating ruthenium, and it may be necessary to include a preliminary step to eliminate ruthenium or to render it nonextractable with the solvent.

Chelate Process. Chelation has been applied to the simultaneous recovery and decontamination of plutonium and uranium on a small scale, but it appears that considerable work is required before a specific process can be devised. The only obvious disadvantage of such a process is the cost of the chelation agent, TTA, although the separation of certain trace compounds such as zirconium may prove troublesome. Otherwise, it is simpler than the Purex process, possibly requiring only a single cycle for plutonium decontamination and a single cycle for uranium decontamination.

Comparison of Extraction Processes. In making a comparison of the four processes, it is necessary to evaluate each of the advantages and disadvantages in terms of the factors (1) capital cost, (2) operating cost, and (3) safety.

The material and labor cost of an extraction plant is largely a fixed cost due to buildings, retention

DECLASSIFIED

basins, laboratory, etc., and only a relatively small portion (about 25 per cent in the case of Redox) is a material and labor cost for process equipment. As a consequence the capital cost will not vary greatly for the four processes. Nevertheless, the capital cost can undoubtedly be reduced if the required number of cycles is low and if the number of preliminary treatments is low.

In the case of the Redox and Purex processes it is probable that two uranium and three plutonium cycles will be required; the Butex process will probably require at least this many cycles and possibly more; the Chelate process possibly may effect the required decontamination in one uranium cycle and one plutonium cycle.

With regard to required feed pretreatment, all processes undoubtedly will require that the solution be filtered to remove silica. Both the Purex and Chelate processes require that the plutonium be reduced to the trivalent state prior to a quantitative oxidation to the tetravalent state. The Chelate process may, in addition, require a zirconium-removal step. The Redox and Butex processes require a feed containing plutonium in the hexavalent state, with the latter probably requiring a step specifically aimed at the removal of ruthenium.

Operating cost is comprised primarily of the following factors: (1) direct labor (dependent upon the complexity of the process), (2) raw materials, and (3) waste volume (the cost of providing waste storage capacity is considered an operating expense at Hanford).

The direct labor cost is thus dependent upon the same factors as is the capital cost. The Purex process is preferable in this respect to Redox and Butex, and the Chelate process, while difficult to evaluate, is probably comparable to Redox.

In regard to raw materials, the Redox process is highly disadvantageous because of the high aluminum nitrate consumption. The Chelate process suffers a serious disadvanatge because of the costly chelation agent. There is little discernible difference between Purex and Butex. The former probably requires more nitric acid, whereas the latter utilizes a more expensive solvent, dibutyl carbitol, and some salt. In view of the facts that Purex will probably require fewer cycles, and hence less chemicals, and that nitric acid is an inexpensive chemical, it seems that Purex has a slight advantage over Butex in this respect.

In regard to the waste volumes, Redox is at a great disadvantage, with the other three processes rated approximately equal.

From the safety viewpoint the use of low-flash-point solvent, as in the Redox and Chelate processes, is a disadvantage. The Butex process uses a small quantity of ammonium nitrate which may be considered hazardous.

In summarizing the relative merits of the several solvent extraction processes each has been rated with respect to six separate characteristics as shown in Table 1. It can be seen that the Purex process rates equal to or better than the other processes in all respects except the questionable possibility of attaining adequate decontamination in the Chelate process with single plutonium and uranium cycles.

Table 1 —Relative Rating of Solvent Extraction Processes

	Purex	Butex	Redox	Chelate
Capital Cost				
Required cycles	2	3	2	1(?)
Preliminary treatment	1	2	1	3
Operating Cost				
Direct labor	1	3	2	2
Raw materials	1	2	4	3
Waste volume	1	1	2	1
Safety	1	3	2	2

Ion Exchange

Ion-exchange methods have been investigated extensively for the recovery of plutonium from irradiated uranium metal. However, the application of ion-exchange methods must be regarded as being in the developmental stage from an engineering point of view.

There are two advantages associated with ion-exchange processes as they have been contemplated thus far:

1. Ion-exchange adsorbents possess marked selectivities for certain ionic species.

2. Certain chemical operations, such as oxidation-reduction, which are usually time-consuming, may be eliminated.

The disadvantages inherent in ion-exchange processes are low capacity of the exchange medium, relatively low flow rates of the process streams to the absorbent, batch processing, large quantities of chemicals required for wash solutions, incomplete separation so that additional purification is required, and possible poor radiation stability of the resins.

Many of the foregoing disadvantages are not important for certain limited applications. For example, if sufficient selectivity were attainable in a continuous process, it might be advantageous to concentrate the bulk of fission products from future plutonium- and uranium-free waste streams on ion-exchange resins and then to elute these resins to provide a concentrated stream of fission products.

This type of application is illustrated partly by the use of ion-exchange resins to scavenge radioactive materials from laboratory wastes at ORNL. Approximately 98 per cent of the activity in these wastes is removed after passage through a column of Dowex-50 resin.

DECLASSIFIED

An example of another potentially important separation process employing ion exchange is the quantitative separation of uranium and protactinium from thorium. Using anion-exchange resins, it has been found possible to remove quantitatively trace amounts of uranium and protactinium from gram amounts of thorium. This specificity is precisely what is needed in a recovery process for materials formed in a thorium blanket of a breeder reactor. If solutions of uranium or thorium can be found which can be circulated through a breeding blanket without excessive decomposition or neutron loss and then passed through an ion-exchange column for recovery of bred material, the attractive possibility of continuous reprocessing of a breeding blanket may be attainable.

DEVELOPMENT OF NEW SEPARATION PROCESSES

Introduction

In the preceding sections separation processes which have been thoroughly investigated were evaluated. In the present section attention is shifted to more novel methods of separation about which less is known but which ultimately may be more desirable than any of those considered heretofore.

Progress in developing new methods of separation has been slow because of the necessity for gearing most of the past activity in this field to the requirements of the Hanford reactor and because of the great emphasis which has been placed on using water solutions as mediums for the isolation and decontamination of reactor products. When these restrictions are relaxed, two new types of processes appear potentially of interest: (1) the dissolution of irradiated slugs in fluorinating agents and the separation of the resultant fluorides by distillation and (2) the separation of the constituents of an irradiated slug while in the form of liquid metal.

Enough is known about the basic chemistry of fluorides of uranium, plutonium, and associated elements to sketch the outlines of several possible fluorination and distillation processes. Development of a feasible and economic process for separating reactor products in the metallic state is more of a gamble but could be desirable when metallic fuel elements are used in a reactor. With such a process chemical costs might be reduced, present metallurgical steps eliminated, and fission-product-waste disposal simplified.

Separation by Fluorination and Distillation

Processes for separating reactor products by fluorination and subsequent distillation are being actively investigated at the Argonne and Oak Ridge National laboratories and at the K-25 plant. Work at these installations has shown that irradiated uranium metal can be converted to a mixture of fluorides by either gaseous fluorine or interhalogen compounds such as ClF_3, BrF_3, or BrF_5. The basic physical chemistry of the fluorides of uranium, plutonium, and the fission products has been under study at these laboratories and at Los Alamos. Many properties of the interhalogen compounds and their mixtures with one another and with inorganic fluorides have been determined at both Argonne and K-25 as well as by workers abroad.

Although knowledge of these mixtures is still far from complete, it is apparent that the chemistry of solutions of inorganic fluorides rival aqueous solutions in versatility and give promise of being mediums in which efficient and economical separations may be carried out. Because of the probability that desirable separation methods using these substances can be developed, we strongly endorse the continuation and extension of these investigations by AEC. With aggressive continuation of such a development, we believe that it might be possible within two years to demonstrate that a fluorination and distillation process for separating and decontaminating uranium and plutonium from irradiated uranium is cheaper and more desirable than any of the aqueous processes now known. The demonstration of a fluorination process in the event that additional Hanford type reactors are to be built would be most advantageous.

Four main advantages of fluorination-plus-distillation processes compared with aqueous processes are:

1. The equipment should be smaller, simpler, and cheaper than in aqueous processes. Fewer columns should suffice for the same degree of decontamination.
2. Operating costs, including the cost of chemicals, should be lower for the fluorination processes.
3. Uranium would be recovered as UF_6, which would be available for direct use in the K-25 plant, instead of as an aqueous solution of $UO_2(NO_3)_2$, which requires several additional chemical operations for conversion to UF_6.
4. Fission products would be recovered in more concentrated form in the fluorination processes so that storage costs would be lower.

Discussion of fluorination processes in this section will assume the same objectives as those currently set at Hanford, i.e., recovery and decontamination of plutonium, recovery and decontamination of uranium, and safe and economical disposition of fission products.

In considering fluorination processes the following general requirements should be kept in mind:

1. The fluorination reaction should be carried out at moderate temperatures. This is desirable from the point of view of imposing a minimum of restrictions upon materials of construction.
2. The reaction should be carried out at pressures above the triple point of UF_6, 22 psia and 147°F, unless the UF_6 is soluble in the fluorinating agent.

DECLASSIFIED

3. The reaction must be controllable in view of the hazardous character of the materials. The rate of reaction should be sufficiently rapid to eliminate the need for unduly large equipment.

4. Inasmuch as the fluorination of uranium metal is extremely exothermic, provision must be made for a cooling system to dissipate the heat of reaction, maintain temperature control, and thus control the reaction rate.

5. The fluorination of the stripped slugs should be conducted in such a manner that the products formed are gases or solvent-soluble substances.

6. Reactants should be radiation-stable, although minor decompositions yielding products which do not interfere with operation can be tolerated.

As the work at Argonne has shown, interhalogen compounds as fluorinating agents, particularly BrF_3 and BrF_5, have the advantage that the dissolution of the slug takes place in a liquid medium at low temperature and at a moderate rate of reaction. Their most important disadvantage is the requirement that facilities for the regeneration of the interhalogen compound must be provided and materials of construction must withstand corrosion both by fluorine and other halogens.

Although the use of fluorine in place of interhalogen compounds is free from these disadvantages, it has others. Experiments conducted at K-25 and elsewhere have shown that the reaction is highly exothermic and may be difficult to control. The uranium slugs may become coated with metallic fluorides, which may hinder the reaction. Nonvolatile fission-product fluorides may remain in the reactor. To circumvent these difficulties the reaction of uranium slugs with gaseous fluorine might be carried out in the presence of a liquid solvent for metallic fluorides which is inert to fluorine. If such a dissolving procedure could be worked out, it would have the advantages of providing better heat transfer, preventing formation of fluoride crusts, and providing a carrier for residual plutonium and heavy fission-product fluorides.

To be suitable for this purpose the solvent should have a boiling point in the neighborhood of the temperature at which fluorine attacks metallic uranium and should have a freezing point below room temperature. The possibility is suggested that SbF_5, with a boiling point of 150°C and a freezing point of 7°C, may be a suitable solvent for this process. It is known that SbF_5 forms a compound with UF_4 and thus may act as a solvent for it.

The value of a practical fluorination process for the separation and decontamination of uranium and plutonium is dependent on the over-all requirements and program of the AEC, and recommendation here can only be made on the basis of technical considerations. It is believed that a research and development program should be supported for the purpose of demonstrating the practicability of a fluorination process.

Research programs should be continued and should cover the following points: (1) determination of the rate of reaction of uranium and lower uranium fluorides with fluorine and BrF_3 and other interhalogens as a function of temperature, (2) determination of solubility data for mixtures of such substances as UF_6, UF_5, UF_4, SbF_5, BrF_5, BrF_3, ClF_3, ClF, Br_2, F_2, and the more abundant fission-product fluorides, (3) determination of the properties of the plutonium fluorides, (4) determination of the chemical and radiation stability of SbF_5 and similar substances and the extent of their reaction with the metal and fluorides of uranium, (5) decontamination of UF_6 by fractional distillation, with and without the addition of a stripping agent such as Freon, (6) reaction of PuF_4 with ClF_3 to produce PuF_6, and (7) vapor-liquid–equilibrium data for UF_6 and fission products.

Some of the above-cited research projects are either in progress or are contemplated at various AEC laboratories.

Liquid-metal Processes

A separation and decontamination process which maintains uranium in the metallic state would greatly simplify processing and make possible a large reduction in the size of equipment. Such a process would comprise melting of the slugs, separation of plutonium, decontamination of the uranium, and recasting of uranium. Project literature (Report UCRL-314) suggests various methods, the most promising of which consists in the following steps: (1) melting of slugs and removal of volatile fission products, (2) treatment of molten uranium with a small amount of an oxide, sulfide, or halide of uranium to form a floating layer containing plutonium and rare earth elements, and (3) treatment of molten uranium with carbon to remove zirconium and columbium.

This scheme has been proposed from thermodynamic considerations and requires experimental evidence to determine its feasibility.

A liquid-metal process could be of great benefit in the development of a breeder reactor. The most critical requirement of a breeder reactor is high recovery in separation processing. Should it be demonstrated that the only possible fuel element for such a breeder is a metallic one and that burn-up is fairly low, then a liquid-metal decontamination and recovery process may be essential. This conclusion is based on the assumptions that very high recovery is probably attainable only with great difficulty if the metal must be converted to a compound and reconverted to metal and that a metallic process possibly could attain the necessary recovery because of the fewer processing steps involved in decontamination.

DECLASSIFIED

At some time it may be necessary to convert U^{235} to plutonium by the use of an enriched fuel element and a blanket of U^{238} instead of by the Hanford type operation using natural uranium. Under these circumstances it may be possible to produce plutonium at lower cost by using a liquid-metal separation and decontamination process instead of the aqueous process presently used.

The fuel element, consisting of enriched U^{235} obtained from the K-25 plant, would be melted, and decontamination would be accomplished by a combination of steps such as volatilization of low–boiling point fission products, slagging of others by addition agents, or extraction with another metal.

Processing of the blanket would be somewhat simpler since the predominant component present in the uranium is the bred plutonium.

If feasible, such liquid-metal processes would eliminate many of the costly operations presently used in production of plutonium from natural uranium.

In view of the uncertainties involved in a metallic process and recognizing the possible advantages of such a process if metallic fuel elements are to be used, it is recommended that limited development be undertaken along such lines that will establish the fundamental characteristics of metallic systems. No large-scale development is recommended until the need for such a process is established or unless fundamental information obtained indicates that such a process has a good probability of competing with other established separation processes.

JOINT DEVELOPMENT OF REACTORS AND SEPARATION PROCESSES

Introduction

Previous sections have considered separation processes devised to suit the requirements of reactors which have been designed without attempting to simplify the associated chemical or metallurgical operations or reduce their cost. In the present section, consideration will be given to the manner in which reactor design and separation-process design may be adapted to one another with a view to reducing their combined cost.

For purposes of this discussion it is convenient to classify nuclear reactors under the three headings "Natural-uranium Reactors," "Enriched Reactors," and "Breeders." This section will be organized under these three principal headings.

Natural-uranium Reactors

All reactors using natural uranium as fuel are necessarily characterized by a low conversion of uranium per pass through the reactor. This arises because the reactor ceases to be critical when the ratio of U^{235} and Pu^{239} to U^{238} drops much below the natural abundance of U^{235} in U^{238} and when the concentration of fission products with large capture cross sections for slow neutrons builds up. This limits the conversion of uranium to the order of one part per thousand per pass. When the reactor produces plutonium for weapons use, the allowable conversion per pass is even lower because of the build-up of undesirable higher isotopes.

With such a low conversion per pass the chemical processing plant for a natural-uranium reactor necessarily handles large quantities of uranium relative to the small amount of fissionable material consumed. It would thus be most desirable to design the reactor and the chemical-processing plant so that the minimum number of operations is needed to convert uranium from one into a form suitable for processing in the other.

It is hard to imagine a combination of reactor and chemical-processing plant which comes further from meeting this condition than does the Hanford installation. The use of canned metallic fuel elements in the reactor and aqueous processes in refining uranium for the reactor and separating the reactor products calls for many costly intermediate operations. There is, of course, good historical precedent for this unfortunate state of affairs. The use of metallic fuel elements for a nuclear reactor has the advantages of minimizing neutron capture by extraneous elements, maximizing the density of the nuclear fuel, facilitating heat transfer, and eliminating chemical-decomposition problems. At the time the Hanford reactors were designed, the difficulties of the nuclear process seemed so formidable that it was essential that the reactor design be facilitated by the use of metal fuel elements, even though chemical processing was to be done in aqueous solution. Nevertheless, this is not a desirable ultimate solution for natural-uranium reactors.

Should additional natural-uranium reactors be built for power production, plutonium production, or both, a strong effort should be made to adapt the requirements of the reactor and the chemical and metallurgical plants to one another. So much more is now known about these two elements of the process that such an effort might well be fruitful. We have considered several alternatives and offer recommendations on some lines of investigation which appear promising and others which do not.

Objectives of Separation Plant for Natural-uranium Reactor. Before considering these alternatives it is important to analyze briefly the objectives of the separation plant associated with a natural-uranium reactor. Whether the reactor be operated primarily to produce power or plutonium, the plutonium will be the most important product of the separation plant. It should be recovered in good yield and with decontami-

DECLASSIFIED

nation adequate for the uses to which the plutonium is to be put. If it is to be used for weapons, the high degree of decontamination now specified will be needed. If it is to be used as reactor fuel, a lower degree of decontamination would suffice if remote fuel preparation methods could be employed.

Recovery of the uranium in good yield and with adequate decontamination is the second objective of the separation plant. If the uranium is to be converted to UF_6 feed for a diffusion plant, the extreme decontamination now specified will be required. If the uranium is to be used in a reactor, either as fuel element, after fortification with enriched U^{235} or plutonium, or in a breeder blanket, a lower degree of decontamination would suffice if remote fabrication methods could be employed.

The third objective of the separation plant is to concentrate the fission products into a form suitable for cheap, safe disposal. This objective is independent of the uses to which the plutonium and uranium are to be put.

Remote Fabrication of Contaminated Reactor Parts. The use of remote methods for fabricating contaminated plutonium or uranium into reactor parts has been mentioned as one possibility for reducing the complexity and the cost of chemical-separation methods. It has been visualized, for example, that the uranium in an aqueous solution of spent slugs could be recovered with only partial decontamination and then converted into metal, formed into slugs, and canned by remote methods. This proposal does not seem attractive to us for two reasons. First, the proposal seeks to simplify only one link in the chain of processes while making several others much more complex and difficult. It seeks to simplify decontamination, which with a good process is already satisfactory, while adding greatly to the cost of preparation of metal and machining and canning of slugs. Second, in the present state of nuclear technology it seems unlikely that a reactor will be run in such a way that both plutonium and depleted uranium would be returned to the reactor; decontamination of one or the other (or both) is likely to be required, and, if one of these reactor products is to be fully decontaminated, the second can be fully decontaminated with little additional trouble or cost. The bases for the opinion that it is unlikely that both plutonium and depleted uranium would be returned to the reactor are that plutonium is more effective than U^{235} as a nuclear explosive, whereas it is substantially on a par as a source of power, and that more efficient use is made of the U^{235} in depleted uranium by separating out the U^{235} by diffusion than by bringing the U^{235} content back to the natural value by the addition of separated U^{235}.

In summary, the development of remote methods of fabricating uranium or plutonium contaminated by beta- and gamma-active material into metal reactor parts is not considered an attractive means of simplifying processes for separating the products of a natural-uranium reactor if aqueous chemical-separation processes are used.

Alternative Fuels. In line with seeking to eliminate chemical and metallurgical operations between the preparation of fuel for a natural-uranium reactor and the separation of the irradiated fuel into plutonium and UF_6, it is evident that there would be a considerable simplification if metallic fuel elements presently used could be replaced by any of the compounds in the normal conversion chain between uranium ores and UF_6. Compounds which should be considered from this standpoint are aqueous solutions of uranium salts, molten uranium salts, solid uranium oxides, UF_4, or UF_6 itself. We have concluded that the solid UF_4 or the solid uranium oxides are the most promising fuels for this purpose.

Aqueous Solutions. The use of an aqueous solution of a uranium salt as a fuel element suggests the attractive possibility of a homogeneous reactor but would give rise to a number of engineering difficulties, mostly associated with the need to use heavy water as solvent and the decomposition of water and salt by radiation. We are informed that at the natural U^{235} concentration use of heavy water as the solvent for uranium salts is necessary if a chain reaction is to be maintained in a homogeneous reactor and that it is probably necessary in a heterogeneous reactor. Experience with the Los Alamos water boiler indicates that a reactor operating at the Hanford level would produce around 100,000 cu ft (standard) of gas per hour by decomposition of the water. Very high recoveries would be required to avoid excessive costs for heavy water make-up.

Another difficulty in using heavy water is the problem of preventing contamination by light hydrogen. If an organic solvent were used in separating uranium and plutonium from a heavy water solution, it would be necessary to guard against exchange of hydrogen between solvent and heavy water.

A third difficulty with such a reactor, common to all reactors using aqueous solutions, is fluctuations in reactivity caused by density fluctuations due to gas bubbles. This can be made less serious by operating under pressure but is troublesome in any event. A serious hazard associated with gas formation is the possibility of explosion of the oxy-hydrogen mixture formed by decomposition of the water.

Taking all these difficulties into account, we have concluded that a normal-uranium reactor using aqueous solutions is not a desirable development venture for the purpose of simplifying the separation of reactor products.

Molten Salts. The number of uranium salts which might be used in the molten state as reactor fuels is severely limited by considerations of melting point, chemical stability, and neutron-capture cross section. The fluorides appear to be the only compounds of this type which have low enough neutron absorption to be used in a normal-uranium reactor. The melting points of the three principal fluorides are UF_4, 980°C; UF_5, about 400°C; and UF_6, 55°C.

Unless a solvent for UF_4 can be found, use of this compound in the molten state is ruled out because of its high melting point. UF_5 is undesirable because of its high dissociation pressure into UF_4 and UF_6, which is around 10 atm at the triple point.

$\underline{UF_6}$. UF_6 as a reactor fuel has been the subject of several reports.[1] Use in the liquid form has the serious difficulty of decomposition into UF_4 and fluorine. Recombination of UF_4 and fluorine is too slow at temperatures below the critical point of UF_6.

Use in the gas phase, at temperatures above the critical, gives rise to other difficulties. It is necessary to use very high pressure in a normal-uranium reactor to obtain a sufficient density of uranium to maintain a nuclear chain reaction. Early experiments have indicated that plutonium, the desired product of the reaction, does not remain in the gas phase and is largely deposited out as solid within the reactor. It is probable that some of the fission products which formed nonvolatile fluorides would also remain in the reactor.

For these reasons we have concluded that the proposal to use molten uranium salts as fuel in a natural-uranium reactor is not an attractive means of simplifying the separation problem.

Solid Uranium Compounds. There is much more promise in considering the use of solid uranium compounds in a normal-uranium reactor than in any of the alternatives considered thus far. The most suitable substances appear to be UF_4, UO_2, or U_3O_8 because oxygen and fluorine have desirably low neutron-capture cross sections. Moreover, use of powdered solids permits greater burn-up because of the lesser problem of mechanical deterioration of fuel elements.

Three ways in which these solids could be used are in sealed cans, in tubes from which they could be intermittently discharged, and in suspension in a gas or liquid which is circulated through the pile. All these alternatives have the advantage of eliminating the need for metal production. An oxide of uranium would be readily adapted to an aqueous separation process. UF_4 would lend itself to the fluorination and distillation type of separation process.

Use of these compounds in place of metal would admittedly change radically the design of a normal-uranium reactor, but this does not seem to be an insuperable difficulty. It might be advantageous to use heavy water as a moderator to keep the reactor from becoming too large. Heat-transfer problems would depend on how the solid was held in the reactor, but they do not appear to be insoluble.

Of the methods proposed for containing the solid in the reactor, the use of a sealed can gives rise to the least number of reactor engineering problems but complicates chemical processing by requiring that the powder be canned before irradiation and the can removed afterwards. An alternative to this would be to contain the solid in vertical tubes, built permanently into the reactor, which could be loaded and unloaded pneumatically or by gravity. It would be necessary to establish the maximum temperature at which such a fuel element could be used without sintering into a mass which could not be discharged from the reactor. It would also be important to establish the proper distribution of solid throughout the tube. A third possibility would be to circulate the fuel continuously through the reactor in suspension in a gas or liquid as a fluidized solid. This is the most radical of the three alternatives and brings with it some troublesome problems in ensuring proper solid distribution and preventing spread of radioactive gases or solid particles.

In summary, it is felt that substitution of UF_4 or uranium oxide for metallic uranium in a natural-uranium reactor would permit desirable simplification in the associated chemical processing without necessarily giving rise to insuperable difficulties in reactor engineering. Should additional natural-uranium reactors be contemplated, we would recommend that studies be made of the use of these solids as fuel elements, considering the alternative methods of containing the fuels which have been suggested.

Enriched Reactors

Separation-process requirements for a reactor whose fuel is concentrated fissionable material are entirely different from those of a natural-uranium reactor. The fractional burn-up of uranium per pass for such a reactor is limited more by physical deterioration of fuel elements than by depletion of fissionable material or nuclear poisoning by reaction products. It is hoped that the Materials Testing Reactor can be run at a burn-up of 10 to 20 per cent of the uranium per pass in place of the 0.1 per cent or less which is possible in a natural-uranium reactor. In the proposed West Milton reactor an equally high burn-up goal has been set. If such high burn-ups are obtained, the rate at which fuel material need be reprocessed is greatly reduced compared to a natural-uranium reactor at the same power level, and the cost of the chemical separation per unit of power is correspondingly reduced. Chemical reprocessing of fuel becomes more of a laboratory operation and less of an engineering problem, and a greater number or complexity of operations is permissible. It has been indicated that high burn-up may be obtained by the expedient of alloying the fissionable material in the fuel element. Under

DECLASSIFIED

such circumstances metallurgical processing of the fuel material is not reduced to the same extent as chemical processing. However, the metallurgical operations will still be considerably smaller than those required for a natural-uranium reactor of the same power level. To this extent the development of economical separation processes for an enriched reactor is less important than in a natural-uranium reactor. However, the recoveries required are higher because of the much greater value of the fuel.

The main objectives of the chemical-separation plant for an enriched reactor are the recovery, decontamination, and fabrication of fissionable material for reuse in the reactor and the packaging of fission products for disposal. The completeness of decontamination required depends on the type of fabrication methods used in reworking the fissionable material.

High Burn-up. The most important means of simplifying separation processing for an enriched reactor is to obtain the highest possible burn-up of fuel. An ideal fuel element would be one which would permit such high burn-up that recovery of fissionable material from spent fuel would not be economically justified. This does not seem to be attainable, but designing for the highest possible burn-up is still of paramount importance.

Even if the assumption be granted that enriched reactors will be designed for high burn-up per pass, the primary requirement of the separation process is high recovery. This can be most easily attained by using as few process operations as possible and, where reactor operation permits, by sacrificing completeness of decontamination for higher recovery. Because of the low throughput, however, it is not important that the separation operations be economical of chemicals.

Fuel Elements. The fuel element of an enriched reactor, which is preferred from the standpoint of facilitating completeness of recovery, is one employing a powdered compound. Metallic fuel elements are undesirable because reprocessing calls for operations which generate considerable scrap such as reduction of salts to metal and casting and machining of metal, all of which make high recoveries difficult. Moreover, the prime factor which made metal fuel elements the best for a normal-uranium reactor from the nuclear standpoint, namely, high neutron economy, is of less importance in an enriched reactor. Liquid fuels are of less potential value in an enriched reactor than in a normal-uranium reactor because the low throughput makes ease of interconverting fuel between reactor and separation plant of secondary importance.

The most desirable way of using a powdered compound in an enriched reactor, from the standpoints of maximizing burn-up and facilitating recovery, would be to contain the powder in the minimum number of individual tubes which could be vented, continuously or intermittently, to discharge gaseous fission products. The use of sealed cans to contain the powder, such as the pins proposed for the West Milton reactor, would be the next most satisfactory way of maximizing burn-up and facilitating recovery. The exigencies of enriched-reactor design, such as the large heat fluxes and necessity for close control of the distribution of fissionable material, might dictate the use of pins, even though the burn-up would be limited by the pressure built up in the pin.

Recovery vs. Decontamination. For either type of fuel element the separation process should consist of a minimum of operations, even at the expense of sacrificing decontamination in order to secure high recovery. It is conceivable that it would be advantageous to reload a partially decontaminated product from the recovery process into the fuel containers by remote means rather than to decontaminate it completely by a process which would entail greater losses.

The considerations of minimizing losses become of crucial importance in breeders, which are discussed in the following section.

Breeders

For purposes of this report a breeder is defined as a reactor which operates with no net loss of fissionable material. The objectives of operating such a reactor would be either to produce power by consuming source material only and with no net loss of fissionable material or to obtain a net gain in fissionable material, or both.

As a means of producing fissionable material without recovering power, breeding is much more costly than a natural-uranium reactor, so that it would not be used for the production of fissionable material except in the event of an extreme shortage of natural uranium. Thus breeding is not likely to be an important operation unless it becomes possible to produce power economically by nuclear fission. Although we are skeptical of the imminence of this development, for the purposes of this section we will assume that the production of power by nuclear fission is economically feasible, and we will examine the separation-process requirements of breeders in relation to this assumption.

The conditions for which the chemical process must be designed depend primarily on the fraction of the fissionable material in the core of the breeder which may be burned up per pass through the reactor and on the amount of source material which may be converted to fissionable material per pass through the reactor.

The degree of conversion in the core which can be allowed without physical deterioration of fuel elements is a very uncertain quantity. In addition, the limitations that must be put on the conversion to achieve good neutron economy are likewise not known reliably.

DECLASSIFIED

As a result widely varying estimates are being offered for the allowable core burn-up. The Experimental Breeder Reactor, for example, has been designed on the basis of a 0.1 to 0.3 per cent burn-up; yet the idea of placing fertile material in the core so that a gross burn-up of over 100 per cent may be achieved has also been discussed. In the face of such uncertainties it is, needless to say, difficult to evaluate the various chemical processes which may be useful in conjunction with a breeder.

Nevertheless a start may be made in considering separation processes for breeders by reviewing what is known about neutron yields for different fission reactions since these, at least, are reasonably well known.

The theoretical upper limit for the net production of fissionable material in a breeder per unit of fuel destroyed is obtained by deducting 2 from the number of neutrons released per atom destroyed. For U^{233} and plutonium these theoretical upper limits are

	Fast neutrons	Slow neutrons
U^{233}	0.56	0.34
Plutonium	0.90	−0.05

In a practical breeder the net production of fissionable material per unit of fuel destroyed will be less than these by the number of neutrons escaping from the reactor, absorbed in structural materials, coolant, controls, etc., or used up in undesirable side reactions. One of the purposes of the Experimental Breeder Reactor is to obtain a measure of the net production of fissionable material in an actual reactor. Until this measurement is available, Zinn's[2] estimate of a loss of 0.24 neutron per atom destroyed due to escape or absorption in structural materials and coolant may be used arbitrarily for purposes of orientation. With such a neutron loss the net gain in fissionable material per unit of fuel destroyed is reduced to

	Fast neutrons	Slow neutrons
U^{233}	0.32	0.10
Plutonium	0.66	−0.29

From these considerations it is apparent that plutonium is the better fuel for a fast breeder and that U^{233} is the only fuel available for a slow breeder. In this section an attempt is made to sketch the material flow quantities which would be handled in the chemical-processing facilities for a fast plutonium breeder and a slow thorium breeder.

To derive these material-flow quantities it is necessary to make assumptions regarding (1) the burn-up per pass through the core, (2) the degree of conversion of source material to fissionable material per pass through the blanket, and (3) the recovery of source and fissionable material per pass through the recovery plant. The allowable burn-up per pass through the core is limited because of the increased absorption of neutrons by fission products accumulating in the core and because of physical deterioration of the core fuel elements. The allowable conversion per pass through the blanket is limited because of the absorption of neutrons by fissionable material bred in the core. So little is now known about these factors that it has been necessary to make rather arbitrary assumptions about them in order to develop illustrative material flow sheets. We have assumed that a recovery of 99.5 per cent of source and fissionable material can be realized in core- and blanket-processing plants.

Material Flow in Breeders. Figures 1 and 2 illustrate the flow of source and fissionable material which has been hypothesized for a fast plutonium and slow U^{233} breeder, respectively. The basis for each flow sheet is 1 mole of fissionable material destroyed in the breeder core.

The fast plutonium breeder consists of a plutonium core from which the maximum possible yield of fast neutrons is extracted for reaction with U^{238} in a physically separate blanket. It has been assumed that a 5 per cent burn-up in the core can be attained through the use of powdered fuel contained in sealed pins or through some other expedient which will permit so high a burn-up without physical damage to the fuel element. That so high a burn-up can be achieved without undesirable absorption of neutrons by fission products remains to be demonstrated.

In the blanket, neutrons react with U^{238} to produce, ultimately, Pu^{239}. One of the greatest uncertainties of such a breeder is the level to which the concentration of Pu^{239} can be allowed to build up before fission of Pu^{239} and conversion of Pu^{239} to Pu^{240} constitute so heavy a drain on neutrons that the net production of fissionable material is seriously lowered. That the 0.05 per cent level shown in Fig. 1 may be permissible is indicated by the capture cross sections for slow neutrons, which are shown in Table 2. If the situation for fast or intermediate neutrons is more favorable, the Pu^{239} concentration in the blanket may be increased to a higher level without excessive loss of neutrons.

In any case it is probable that the blanket-processing plant will have to handle much more material than the core-processing plant and will add more to the cost of the installation. The requirements of the core-processing plant are stricter, however. Because it handles the bulk of the fissionable material, it is more important that high recoveries be attained here than in the blanket-processing plant.

The slow U^{233} breeder that is shown in Fig. 2, designed for a more optimistic burn-up of 20 per cent,

DECLASSIFIED 715 096

should make much less exacting demands of its chemical and metallurgical facilities than would the fast plutonium breeder shown in Fig. 1. To this end, the core fuel elements would consist of U^{233} diluted by 80 times its weight of thorium. Since the relative quantities of these elements are in the inverse ratio of their neutron-capture cross section, there will be no net gain or loss of U^{233} in the core because it will be produced from thorium as fast as it is burned up. For every atom of U^{233} undergoing fission, about 0.1 slow neutron will be available for reaction with thorium in the blanket, the remainder having reacted with thorium in the core. In this type of breeder the blanket is a relatively unimportant component, acting as an economizer for neutrons instead of being the main site of production of fissionable material, as in the fast plutonium breeder previously considered.

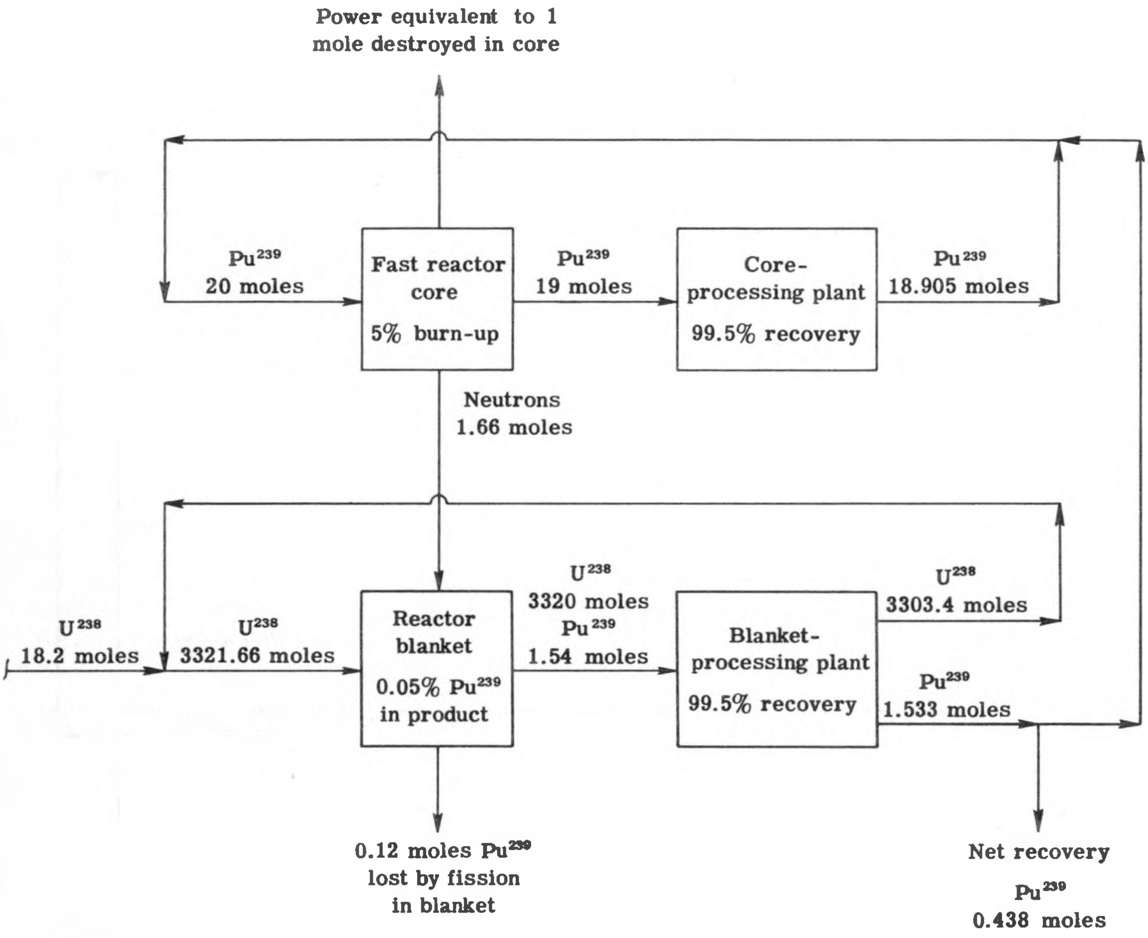


Fig. 1—Material flow in fast plutonium breeder.

It has been assumed that a burn-up of 20 per cent of the U^{233} per pass through the core can be achieved, owing to the considerable dilution of fissionable material by thorium. The concentration of U^{233} in thorium at which it will be desirable to reprocess the blanket is much less critical than in the case of the fast plutonium breeder because of the more favorable ratio of neutron-capture cross sections for the formation of U^{233} compared to its destruction (see Table 3).

In any event the blanket-processing plant would be only a minor auxiliary to this type of U^{233} breeder instead of being the major facility, as in the fast plutonium breeder. The core-processing plant, on the other hand, treats more total material than the core-processing plant of a fast plutonium breeder but less fissionable material. All factors considered, the processing plants of a U^{233} breeder are much smaller and

DECLASSIFIED

less exacting than those of a fast plutonium breeder designed to produce the same amount of power. When the comparison is made for the same net rate of breeding, the processing plants of the two types of breeder are of the same order of magnitude.

In concluding this discussion of material flow it may be of interest to compare these two breeders with a Hanford type reactor in which fissionable material is burned up at the same rate. Table 4 brings out the fact that a Hanford type reactor produces more plutonium than the fast plutonium breeder at a given rate of burn-up, but, of course, it uses up much more source material. The chemical processing facilities of a breeder producing plutonium handle about the same amount of uranium as a Hanford reactor, but they handle more plutonium and must attain a higher recovery. The slow thorium reactor doing most of its breeding in the core has much smaller processing facilities than either a Hanford reactor of the plutonium breeder operated at the same burn-up rate.

It should be emphasized that any favorable representation of these two breeder schemes is based upon the optimistically high core burn-ups which were assumed for them.

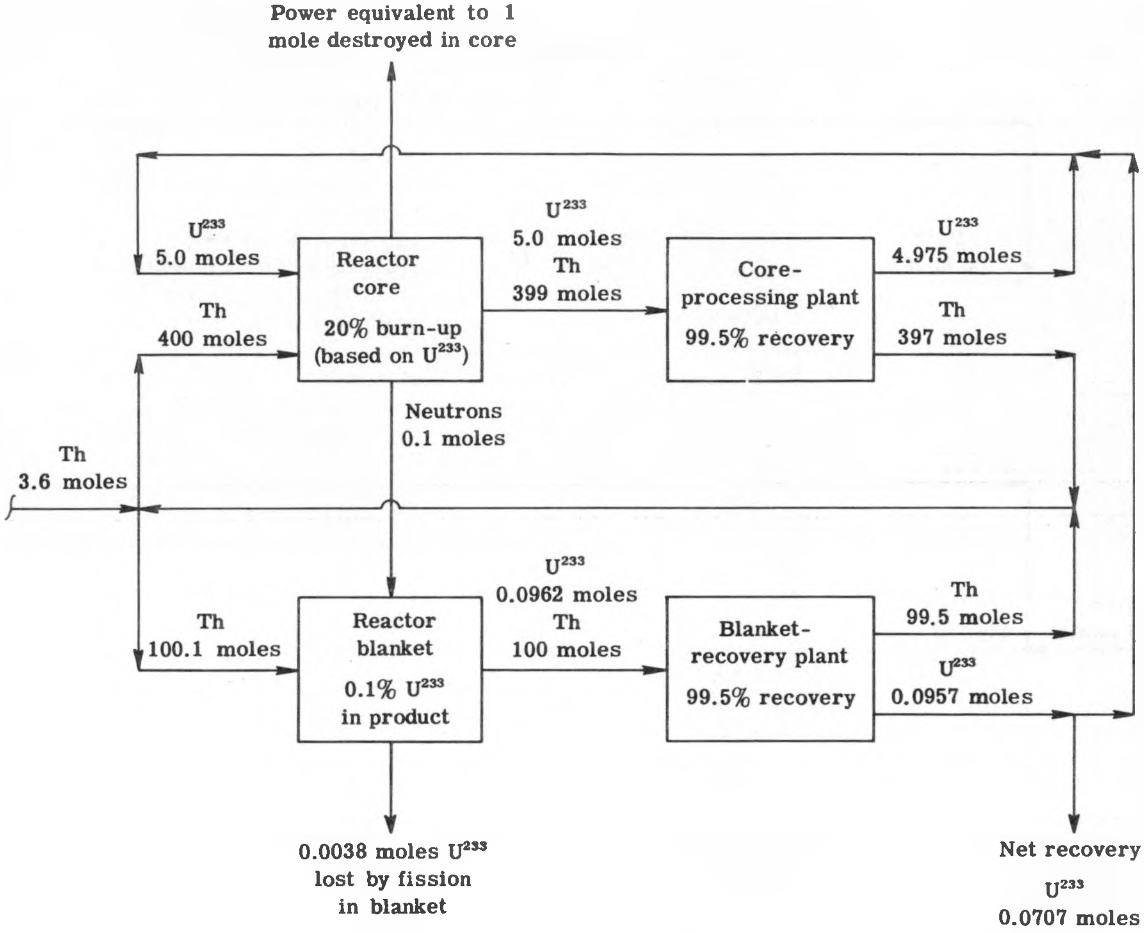


Fig. 2 — Material flow in slow U^{233} breeder.

This discussion of material flow in breeders will have served to bring out the importance of designing such reactors for the maximum possible burn-up per pass of fissionable material through the core and for the maximum amount of breeding in the core and the use of core materials and associated recovery plants which facilitate the high recovery of fissionable material needed for successful breeding. It has been our observation that insufficient emphasis in breeder development has been given to these factors, while at-

DECLASSIFIED

C98

tention has been concentrated on the problems of the reactor itself without regard to the feasibility of the recovery operations. On the following pages we seek to point out the advantages of certain types of core or blanket elements and certain separation processes in facilitating recovery operations in breeders. The fast plutonium breeder is taken up first, followed by the slow U^{233} breeder.

Table 2—Capture Cross Sections for Slow Neutrons

Reaction	Cross section, barns
$U^{238} \rightarrow U^{239}$ (Pu^{239})	3
$Pu^{239} \rightarrow$ fission	750
$Pu^{239} \rightarrow Pu^{240}$	350

Table 3—Capture Cross Sections for Fast Neutrons

Reaction	Cross section, barns
$Th^{232} \rightarrow Th^{233}$ (U^{233})	7
$U^{233} \rightarrow$ fission	500
$U^{233} \rightarrow U^{234}$	50

Fast Plutonium Breeder. For the use of a fast plutonium breeder the same general principles apply to recovery processes as apply to an enriched reactor, discussed in the section on enriched reactors. It is imperative that the maximum possible burn-up per pass consistent with neutron economy, be secured. The burn-up of 0.1 to 0.3 per cent anticipated in the Experimental Breeder Reactor is undesirably low, since it would call for recoveries of 99.97 per cent in the core-processing plant to keep plutonium losses below 10 per cent of the plutonium burned up. The use of an oxide or fluoride in place of metal in the core of such a breeder would greatly simplify the core-reprocessing process by eliminating reduction to metal and casting and machining operations.

The principal novel separation-process requirements introduced by the fast plutonium breeder are in the blanket-processing plant. Any measures that can be taken to run this separation plant at a low plutonium concentration, and thus at a higher uranium throughput, add to the efficiency of the breeding process by reducing the amount of plutonium destroyed by fission or converted to Pu^{240} in the blanket.

These requirements of returning uranium to the blanket in the same form in which it was withdrawn and seeking to operate at the lowest possible concentration of plutonium point to the desirability of devising a process in which the plutonium could be continuously extracted from the material of the blanket without chemically changing the uranium. The ideal process would be one which distilled or leached the plutonium from the blanket as fast as formed without removing the uranium, but a feasible process of this type has not been suggested. Another practicable possibility would be to have the uranium in the blanket in the form of a liquid solution and to continuously or intermittently extract the plutonium from it. The use of a liquid alloy of uranium in a low-melting metal coupled with an extraction process which transferred plutonium selectively to a second liquid phase would be a desirable means of processing this material. On the other hand, the use of aqueous solutions or molten salts to carry uranium in the blanket gives rise to the same problems of chemical decomposition as were mentioned in connection with the use of these liquids in a natural-uranium reactor.

A less radical proposal to simplify blanket processing in a plutonium breeder is to use UF_4 in the blanket coupled with a fluorine separation process or uranium oxide coupled with an aqueous separation process. These measures would have the same advantages as were noted for the normal-uranium reactor, i.e., eliminating the need for reduction of salt to metal and the casting and machining of metal. In a breeder blanket, when a higher recovery is desirable, the use of these compounds in place of metal would be even more advantageous than in a normal-uranium reactor.

U^{233} Breeder. We have seen that the recovery operation in a U^{233} breeder designed for power production only may be greatly simplified by doing as much breeding as possible in the core and aiming for the highest possible burn-up in the core. If these objectives can be attained, the requirements of recovery operations can be made much less stringent than in a plutonium breeder. Nevertheless the same principles that have been found advantageous in separation problems previously discussed apply here also. The use of a liquid alloy of thorium and uranium and a low melting metal in the core, coupled with partial extraction of fission-product poisons by a molten salt would be a very desirable way of keeping the core metal clean enough to maintain breeding without the necessity for converting either the thorium or U^{233} to other chemical forms.

An alternate way of simplifying reprocessing of fuel elements would be to use a solid-metal core and, when this deteriorated mechanically or became poisoned with fission products, to recast the metal under a flux which removed most of the fission products, and to refabricate the fuel elements by remote methods. Another alternative would be to use tetrafluorides or oxides in the core of such a breeder, with the same advantages that have been cited for substituting these compounds for metals in other reactors.

The blanket of a U^{233} breeder lends itself to desirable process simplifications more readily than any reactor material we have considered heretofore. This is because of the great difference in volatility between nonvolatile ThF_4 and gaseous UF_6, which can be taken advantage of in a number of reprocessing schemes. The simplest method, which would involve the least development, would be to use ThF_4 as blanket material, remove it intermittently as the U^{233} built up, and convert the uranium to UF_6 by fluorine or interhalogen compounds. The proposal, which is under investigation at Brookhaven, to remove the uranium from the blanket in place by volatilizing it out with fluorine is more radical but is an even more clean-cut way of recovering uranium from such a breeder. In fact if this process can be perfected so that the uranium can be removed before it builds up in the blanket to a concentration over a few hundredths of a per cent, the simplicity of this operation in a U^{233} breeder compared with the difficult separation job in the blanket of a plutonium breeder may make a fast U^{233} breeder more attractive than a fast plutonium breeder for net production of fissionable material despite the lower neutron yield. Because of its potential value, we would recommend that small-scale experimental work designed to test the feasibility of this process be continued and that collaboration be established between groups working on this process and those considering breeders so that the economic possibilities of a U^{233} breeder in which this recovery process is used may be evaluated.

Integration of reactor and separation-process development is the direction which must be taken to establish, if possible, an economical means of producing power from nuclear fission.

ACKNOWLEDGMENTS

It is a pleasure to acknowledge the valuable assistance and cooperation extended by the Washington office of the Atomic Energy Commission and by Commission and operating personnel at the New York Operations Office; the Brookhaven, Argonne, and Oak Ridge National Laboratories; the Knolls Atomic Power Laboratory; the Gaseous Diffusion Plant; and the Hanford Works. We regret that it has not been practicable in this report to acknowledge the individual contributions of the many scientists and engineers responsible for the development and application of the processes described.

REFERENCES

1. D. E. Hull, Stability of UF_6 in a Pile, Report MonN-268, Mar. 4, 1947, and Possible Applications of UF_6 in Piles, Report MonN-336, July 1, 1947.
2. W. H. Zinn, H. V. Lichtenberger, M. Novick, Report ANL-4356, Oct. 14, 1949.

July 1950

DECLASSIFIED

LYOMETALLURGY: A NEW METHOD OF EXTRACTING URANIUM FROM ITS ORES

By A. M. GAUDIN, F. W. BLOECHER, JR., JOHN
DASHER, DAVID KAUFMAN, PAUL GALVANEK, JR.,
and WILLIAM V. WARD

MIT Mineral Engineering Laboratory
Watertown, Massachusetts

Report MITG-260

ABSTRACT

Lyometallurgy is a metallurgical leaching process in which an organic solvent, initially free of a separate water phase, is used to leach a dry or slightly damp solid. Because of the solubility characteristics of uranyl nitrate, most of the test work has been done with ethyl ether and nitric acid. Most of the laboratory work to date has been concerned with testing the efficacy of lyometallurgical leaching on a large number of uranium-bearing raw materials and plant products. Consequently, a good deal of study has been devoted to the matter of pretreatment and leaching, but not too much effort has been spent on the study of solvent stripping, regeneration, and reagent recovery. Results of lyometallurgical investigation have shown that the method is an attractive alternative to acid leaching for beneficiation of uranium ores. Various flow sheets are given, and some over-all process cost estimates are made.

INTRODUCTION

Most uranium ores, particularly the low-grade domestic ores, are difficult to concentrate by physical means, and since uranium is a slag-forming element it cannot be separated from low-grade siliceous ores by smelting. Most of the work of the MIT Mineral Engineering Laboratory on the treatment of uranium ores has been devoted to hydrometallurgical leaching,[1,2] a well-understood branch of extractive metallurgy in which water serves as the primary solvent. An alternative method that has been tested has been termed "lyometallurgy."

Lyometallurgy is a metallurgical leaching process in which an organic solvent, initially free of a separate water phase, is used to leach a dry or slightly damp solid. The solid may, or may not, have received prior treatment by roasting or acid digestion, and the solvent may, or may not, contain a dissolved acid, such as nitric acid. Lyometallurgy is a coined word, the prefix "lyo-" coming from the Greek word λυειν (lyein) meaning to loose or dissolve.

Unlike hydrometallurgy, lyometallurgy is a relatively new process about which little is known, but it has broad potentialities owing to the wide latitude available in the selection of solvents. Lyometallurgical leaching has thus far been almost exclusively confined to the problem of recovering uranium from its ores. The process is so versatile, however, that uranium recovery may be only one of many applications.

HYDROMETALLURGY VERSUS LYOMETALLURGY

Lyometallurgy, like hydrometallurgy, involves selective extraction of a solid by a liquid, followed by a

DECLASSIFIED

thickening or filtration step to separate the liquid from the solid residue. Thickening is the process of allowing suspended solids to settle so that the solvent can be removed by decanting the clear supernatant liquid. The ease with which thickening and filtering can be carried out depends upon a number of factors, among which are viscosity and surface properties of the solvent, dissolved salts present, and the extent to which the solids in suspension are attracted to, or repulsed by, other suspended particles or the individual molecules or ions of the solvent. Table 1 is a comparison of various properties of water, ethyl ether, and acetone, including some of the properties which have an effect on thickening and filtration rates. The thermal properties of the solvents are also included to indicate how readily the organic liquids can be recovered through application of vacuum or heat.

Table 1 — Some Properties of Solvents

	Water	Ethyl ether	Acetone
Specific gravity	1.00	0.714	0.792
Boiling point at 760 mm Hg, °C	100	34.6	56.5
Viscosity at 20°C, centipoises	1.01	0.23	0.33
Relative polarity	High	Least	Greater than ether
Surface tension at 20°C, dynes/cm	72.8	17.0	23.7
Specific heat at 20°C, cal/g/°C	1.00	0.54	0.53
Heat of vaporization at the boiling point and at 760 mm Hg pressure, cal/g	539	84	125
Solubility at 20°C			
Solvent in water, g/100 ml		7.5	Infinite
Water in solvent, g/100 ml		1.35	Infinite
State of aggregation of suspended solids	Variable, flocculated to dispersed	Usually flocculated	Usually dispersed

Table 2 — Comparative Filtration Rates of Lyometallurgical and Hydrometallurgical Leach Pulps

Ore	Type of leach	Over-all filtration rate, gal/sq ft/24 hr*	Relative rate
Marysvale†	Hydrometallurgy with H_2SO_4 solution	17.4	1
Marysvale	Lyometallurgy with nitric acid–ether solution (10 vol. % acid)	4,750	273
Hite‡	Hydrometallurgy with H_2SO_4 solution	6.63	1
Hite	Lyometallurgy with nitric acid–ether solution (10 vol. % acid)	4,640	700
Hite	Lyometallurgy on damp sulfated ore with 1 to 1 acetone-ether solution	10,700	1,610

*Includes two displacement washes of 1-in. filter cake; vacuum was 20 in. Hg.
†Vanadium Corp. of America partly oxidized ore from Marysvale, Utah.
‡Cupriferous uranium ore from Hite, Utah.

It is much easier to separate a polar solid, such as a finely divided siliceous uranium ore, from a nonpolar solvent like ethyl ether than it is to separate the same solid from a polar solvent like water. In fact, the difference is often so marked as to appear to be a difference of kind rather than of degree. Filtration rates have been compared under conditions of similar cake thickness and similar vacuum (1-in. cake and 20 in. Hg) on an aqueous sulfuric acid leach, and a lyometallurgical leach in ethyl ether (10 vol. % nitric acid) on −20-mesh uranium ore from Marysvale, Utah. The data are summarized in Table 2. The ether filtration rate was 273 times faster than the hydrometallurgical filtration rate. In a similar comparison under the same conditions of vacuum and cake thickness on a −20-mesh cupriferous uranium ore from Hite, Utah, the spread was even greater, being of the order of 700 to 1. Although no quantitative filtration data have been collected for lyometallurgical leaches in which acetone alone was used as the solvent, it has been qualitatively observed that the rate is slower than the ether rate but not so slow as the water filtration rate. However, it turns out that when a mixed solvent, 1 to 1 acetone – ethyl ether, is used to leach a damp sulfated sample of the Hite cupriferous uranium ore the filtration is faster than ever, actually 1610 times faster than the hydrometallurgical rate and approximately twice as fast as the plain ether rate. These data are also shown in Table 2. Thickening rates in organic liquors are likewise much faster than in aqueous solution, relative rates being of the same order of magnitude as the relative filtration rates shown in the last column of Table 2.

In the aqueous leaching of ores that contain finely dispersed clay slimes, thickening and filtration can be quite slow and expensive. There are no such problems in lyometallurgical leaching when solvents such as ethyl ether are used.

A glance at Table 1 shows that the specific heat, heat of vaporization, and boiling point of ether and acetone are considerably lower than those of water. These properties are reflected in another advantage of lyometallurgical leaching: the ease of recovering the solvent for reuse. Lyometallurgical filter cakes, for instance, can be stripped of solvent almost completely merely by vacuum flashing. Actually, the expense of recovering water for recycling in hydrometallurgical operations is much greater than the cost of using fresh water; therefore there are no operations where water is recovered from leach residues. The cost of organic solvents, however, requires almost a 100 per cent recycling of solvent. Preliminary laboratory tests have shown that well over 99 per cent of the organic solvent used can be recovered for recycling.[3] Those tests were run on a small-scale laboratory basis, and a large-scale operation would probably reduce solvent losses even further.

Although the cheapness of water in some areas may outweigh some advantages of lyometallurgy outlined above, the fact that many domestic uranium prospects are located in arid desert regions far from road or railhead changes the situation somewhat. In some regions a water supply may have to be created at the mill, and this is expensive, particularly for small-scale operations. Or the mill site would be selected on the basis of availability of water, at the expense of other factors.

Roads in desert mining regions are rudimentary, consisting largely of the beds of dry streams between steep canyon walls. No matter what the method of ore treatment, haulage costs will be high. The ease of solvent recovery in lyometallurgical operations would mean that the amount of supplies it would be necessary to haul would be relatively small, consisting of reagents and fuel consumed in the processing and food and water for domestic purposes. The small size of the equipment required, because of the ease of filtration and short leach times, might even warrant use of a portable lyometallurgy plant that could travel from mine to mine treating stock-piled ore. At any rate, under desert conditions with high haulage costs and scarcity of water, the ease of solvent recovery and the small size of the plant required make lyometallurgy an interesting alternative method for beneficiating uranium ores.

In addition, choice of a suitable organic solvent permits a much more selective dissolution of the uranium minerals than occurs in aqueous leaching.

DEVELOPMENT OF LYOMETALLURGY

Early work on lyometallurgy was concerned with recovery of uranium from the Witwatersrand (South Africa) gold tailings and high-grade Eldorado pitchblende concentrates.[3,4] Initial work on the Rand materials was directed toward upgrading alkali precipitates from acid liquors obtained by hydrometallurgically leaching Rand cyanide residues. The method involved digestion of the precipitates with nitric acid to convert the uranium to uranyl nitrate, followed by leaching of the damp or dried acid-digested residue with ethyl ether to extract the uranium. The high cost of nitric acid made it imperative that nitrate be recovered from leach residues obtained by this method.

Promising results with the prior nitric acid – digestion method on both Rand precipitates and Eldorado pitchblende led to experimentation with simultaneous nitration-leaching, that is, leaching with a solution of nitric acid in ethyl ether. Elimination of both the prenitration and the drying steps simplified the process. In this method it was found that the amount of nitrate appearing in the tailing was sometimes too small to justify its recovery.

The relatively high price of nitric acid makes the prenitration method unattractive for many low-grade ores, and some of these ores do not respond to direct leaching with nitric acid – ether solutions. It is therefore gratifying and perhaps useful to find that many ores become amenable to leaching with nitrated ether after preliminary digestion with sulfuric acid. In addition, leach residues from this process contain very little of the total nitrate in the system, so that good economy in the use of nitrate is indicated.

From the standpoint of historical sequence lyometallurgy processes for uranium extraction can then be arranged into three categories: (1) leaching after nitric acid digestion, (2) direct leaching with a nitric acid – ethyl ether solution, and (3) leaching after sulfuric acid digestion. Figure 1 contains diagrammatic flow sheets showing the three lyometallurgical processes as they have been used for treating uranium-

DECLASSIFIED

bearing materials, both ores and plant products. Later sections of this article include discussions of various steps in each process.

URANIUM RECOVERY

After leaching, the pregnant solvent can be separated from the residue by filtration or decantation, and the cake can be washed until all dissolved uranium is removed. Two displacement washes of the filter cake have been found adequate. The uranium in the pregnant liquor can be recovered in a number of ways, including (1) evaporating the solvent to dryness, (2) stripping with water, followed by precipitation from the water, or (3) direct precipitation from the solvent with gaseous ammonia. The first method may involve special hazards because of possible peroxide formation. It has not been studied. The second method involves several steps as well as the possibility of losing solvent by solution in the water, and it negates most advantages of the lyometallurgy process. In addition, it would not be suitable for stripping uranium from the mixed solvents used in damp leaching of sulfated pulps. It has therefore been disregarded. Method 3 is attractive; it has been tested on a small scale in the laboratory and is discussed briefly in another section. Figure 2 shows in simplified flow sheet form these three alternative methods of recovering uranium from the solvent.

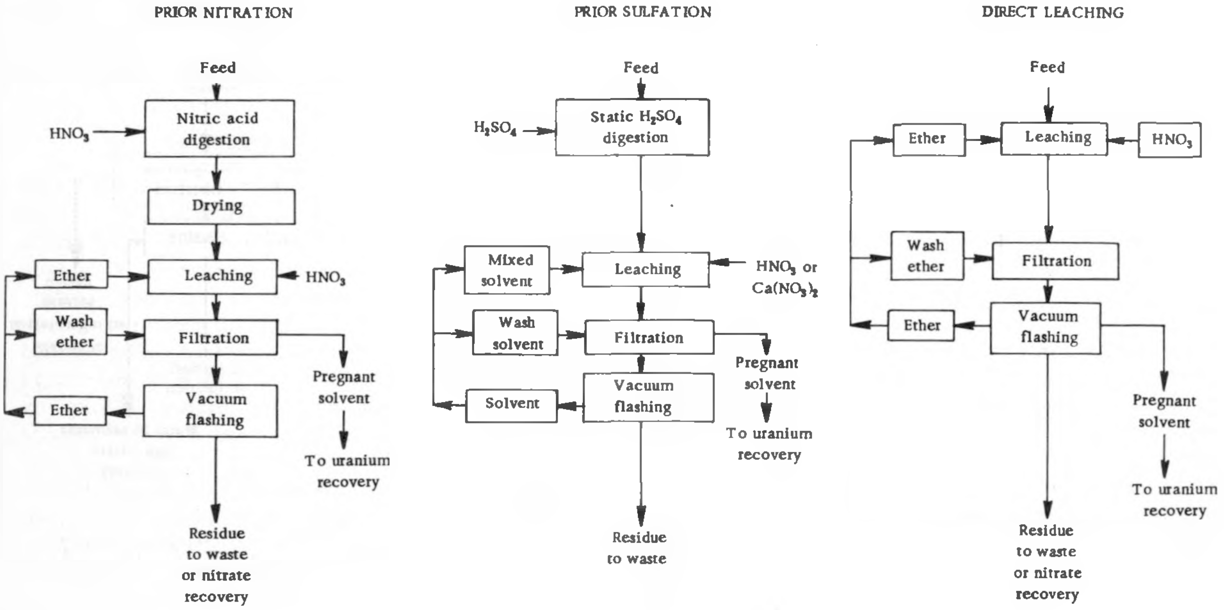


Fig. 1—Flow sheets of lyometallurgical processes for treating uranium-bearing materials.

LABORATORY APPARATUS

Figure 3 is a sketch of the glass apparatus in which most agitation type leaches have been carried out. From 10 to 100 g of solid are placed in the leach chamber, and the apparatus is assembled. Solvent is introduced through the side arm, and leaching is carried on for the desired period of time. During leaching the air vent and the stopcock below the frit are closed. The condenser on the side arm, cooled by an ice cube, prevents loss of solvent. Agitation is accomplished by means of the stainless steel stirrer attached through the packing gland to a small electric motor. At the end of the leach the agitator is stopped and the solvent is withdrawn into the calibrated receiver by opening the stopcock below the frit. Application of a slight vacuum will reduce the time needed for filtration to a few seconds. The cake is usually displacement washed with plain solvent. The pregnant liquor and washes are evaporated over water, and aliquots of the water solution are analyzed fluorimetrically for uranium to determine results of the leaching step. The evaporation over water is merely a laboratory convenience, and in a large-scale operation the pregnant liquor probably would be stripped of values with ammonia gas.

In most tests, including those described in this article, the leaching was carried out for 1 hr using 1.5 to 3 ml of solvent per gram of material leached and roughly the same amount of wash solvent. Little advantage was found in using leach times over 1 hr; in fact, satisfactory extractions were often obtained in 10 to 15 min, as compared to the 24-hr leaches usually justified in hydrometallurgical operations.

PRIOR-NITRATION METHOD

The nitric acid digestion was usually carried out by heating the uranium-bearing material with concentrated nitric acid at a temperature of 80 to 90°C for 1 to 2 hr. The digested material was then dried, pulverized, and leached. Some attempts were made to leach damp nitrated materials without first drying them. Recoveries were good, but it was difficult to get proper mixing. Therefore this modification of the prior-nitration method was not investigated extensively. More work in this direction might be rewarding. In the prior-nitration process the solvent used need contain little or no nitric acid.

Typical results[3-6] are summarized in Table 3. The extractions obtained on pitchblende concentrates, Rand precipitates, carnotites, and other materials were usually good, but the amount of nitric acid required was high since it reacted not only with the uranium but also with other oxides and sulfides. The reagent consumptions listed are based on the assumption of a recovery of 90 per cent of the nitric acid and 99 per cent of the solvent for recycling.[3] The nitric acid would be recovered by a two-step operation consisting in decomposition by heat of the nitrate in the tailings and that washed out of the ammonia precipitate and scrubbing of the evolved gases with water. Condensers and a sealed system would keep solvent losses at a minimum.

On high-grade materials, such as the pitchblende concentrates, recovery of nitrate from the leach residues looks good. For most low-grade materials, where the weight of residue to be heated would be large compared to the amount recovered, the recovery of nitrate from the tailings does not seem practical.

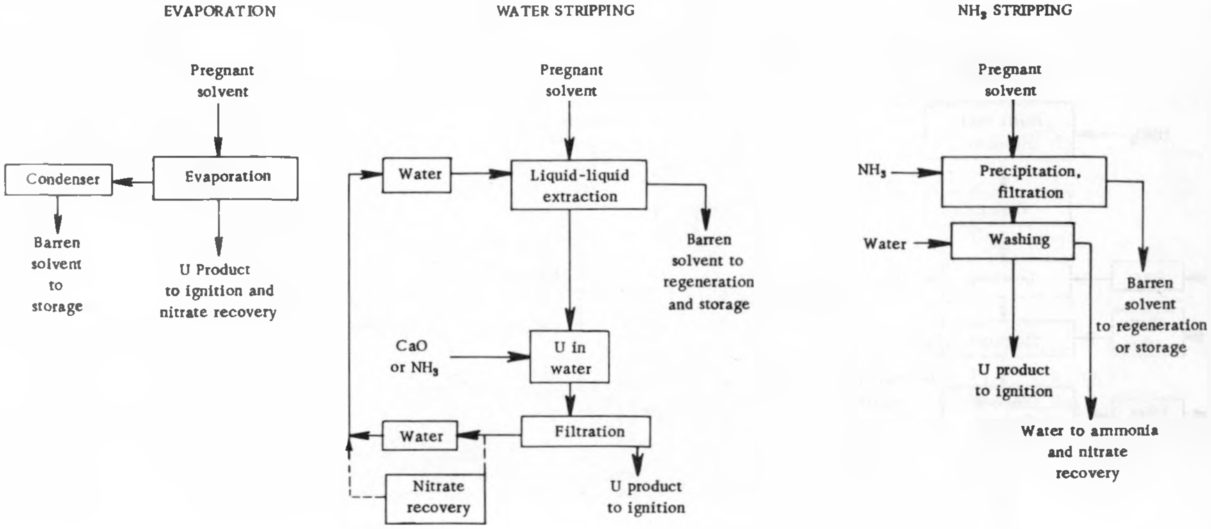


Fig. 2— Flow sheets showing several methods for stripping pregnant solvents of uranium.

DIRECT LEACHING METHOD

The successful treatment of uranium-bearing materials by the prior-nitration method led to experimentation with simultaneous nitration leaching using a solution of nitric acid and ethyl ether. This method is, of course, simpler and in many cases effects economies in nitric acid consumption through selective nitration of the uranium. Consequently, considerably less nitrate appears in the leach residues. Some typical results obtained are summarized in Table 4. Reagent consumptions are again based on the assumption of 99 per cent ether and 90 per cent nitric acid recovery for recycling.

Uranium extractions are generally high from chemical precipitates and from some ores containing secondary uranium minerals. Extraction of uranium from materials containing carnotite, pitchblende, or uraninite is somewhat poorer.

PRIOR-SULFATION METHOD

Materials which were refractory in their response to direct leaching and those low-grade ores for which

DECLASSIFIED

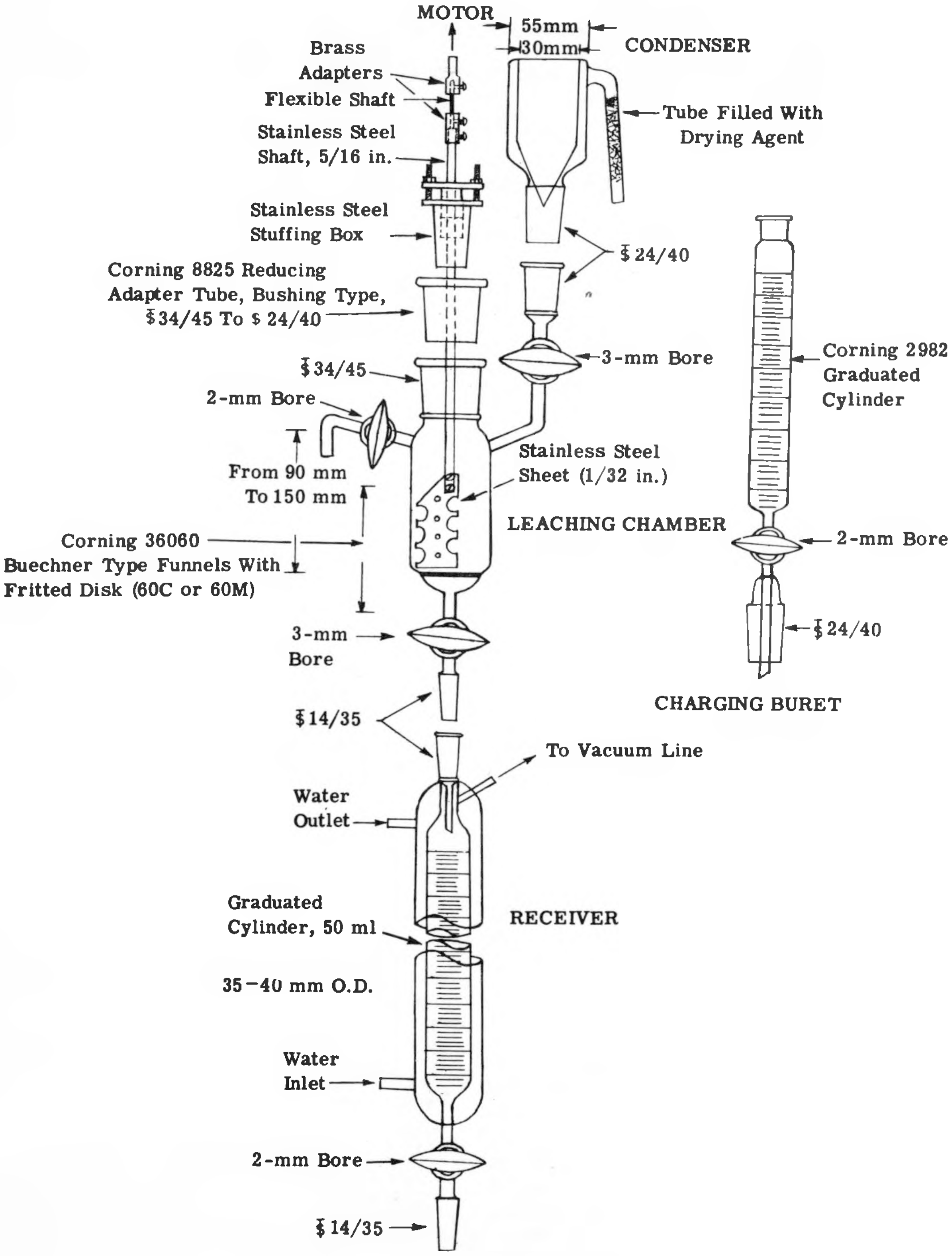


Fig. 3— Laboratory-scale lyometallurgy equipment.

TII 106

DECLASSIFIED

direct leaching resulted in rather high nitric acid requirements per pound of U_3O_8 recovered can be leached more economically after digestion with sulfuric acid. Most tests using the sulfuric acid pretreatment were made on the relatively low-grade carnotites since these were not leached readily by the direct method.

Table 3—Some Typical Prior-nitration Leach Data

Material	U_3O_8,* %	Acid in solvent†	Reagent consumption,‡ lb/lb recovered U_3O_8 Nitric acid	Ether	U_3O_8 extraction, %	U_3O_8 in tails, %
Wild Steer carnotite	0.35	2	4.9	10	89.5	0.041
Eldorado pitchblende concentrate	8.0	2	2.0	1.1	94.7	0.42
Congo pitchblende concentrate	58.4	2	0.20	0.05	98.8	1.43
CX precipitate§	32.0	2	0.20	0.20	98.0	0.70
Rand acid leach precipitate	2.12	0	3.5	7.1	95.3	0.099
Roasted Sunshine ore¶	0.37	2	14	21	91.4	0.032

*Before nitration.
†Vol. % concentrated nitric acid in ethyl ether.
‡Assuming recovery of 99 per cent of solvent and 90 per cent of nitric acid for recycling.
§Congo lime precipitate.
¶Sunshine Mine, Idaho.

Table 4—Some Typical Direct-leach Data

Material	U_3O_8, %	Acid in solvent*	Reagent consumption,† lb/lb recovered U_3O_8 Nitric acid	Ether	U_3O_8 extraction, %	U_3O_8 in tails, %
Wild Steer carnotite	0.35	10	16	7.3	57.2	0.15
Wild Steer carnotite	0.35	5	14	14	34.5	0.23
CX precipitate‡	32.1	10	0.19	0.12	99.5	0.25
Congo pitchblende concentrate	58.4	10	0.26	0.16	28.2	54
Rand acid leach precipitate	2.29	5	0.96	2.4	97.2	0.07
Rand cyanide residue	0.025	10	130	110	64.0	0.0082
Marysvale, Utah, ore:						
Bullion Monarch, oxidized	0.11	10	23	27	77.6	0.026
VCA, primary ore	0.23	10	10	11	92.0	0.017
Utah Cu-U ore, Hite Mill feed	0.30	10	10	9.7	92.8	0.022

*Vol. % concentrated nitric acid in ethyl ether.
†Assuming recovery of 99 per cent of solvent and 90 per cent of nitric acid for recycling.
‡Congo lime precipitate.

Exploratory tests had indicated that, although uranyl sulfate was almost insoluble in ethyl ether, good extractions of uranium could be obtained by leaching the sulfate with ether containing nitric acid. In the earliest tests with sulfuric acid pretreatment, the solids were digested by pulping in a cold dilute sulfuric acid solution at approximately 50 wt. % solids for several hours. The digested pulp was then dried and leached with a nitric acid–ether solution.[5,7] However, it was found that the sulfuric acid pretreatment was just as effective if carried out statically in thick slurries containing 80 to 90 wt. % solids. By leaching with a mixed solvent, such as acetone-ether or alcohol-ether, the drying step could be eliminated. The alcohol or acetone picked up moisture from the ore and facilitated thorough mixing. If the damp pulp were leached with only a single solvent, such as ether, the sticky, pasty character of the pulp prevented proper mixing and washing. If acetone or alcohol were used alone, the leaching was neither as good nor as selective in regard to uranium extraction. Also, the filtration rates, if acetone and alcohol were used alone, were not as fast as the ether rate.

DECLASSIFIED

Tests on the carnotites showed that uranium extraction could be increased if lime, or some calcium salt, were added to the pulp before leaching. In addition, if the sulfated carnotites were mixed with solid calcium nitrate [$Ca(NO_3)_2 \cdot 4H_2O$] instead of lime, the leaching could be done with solvent containing little or no nitric acid, and very little nitrate appeared in the leach tailings. The calcium nitrate appears to react with excess sulfuric acid or uranyl sulfate to form gypsum and to liberate nitric acid and uranyl nitrate which dissolve in the solvent.

Table 5 — Some Typical Prior-sulfation Leach Data

Ore	U_3O_8, %	Type leach	Reagents added, lb/ton of ore					Reagents used, lb/lb recovered U_3O_8†					U_3O_8 Extraction, %	U_3O_8 in tails, %
			H_2SO_4	CaO	Calcium nitrate	Nitric acid	Solvent*	Ether	Acetone	Nitrate	H_2SO_4	CaO		
Indian Reservation carnotite	0.18	Dry	126			190	5	16.2		8.7	57.3		61	0.064
	0.18	Dry	100			190	5	11.0		5.7	37.6		93	0.0059
	0.18	Dry	78			190	5	12.2		5.9	30.9		90	0.010
	0.18	Dry	126	50		190	5	11.6		5.5	36.4	14.5	96	0.010
Gypsum Valley carnotite	0.60	Damp	200			190	5	2.5	1.0	2.0	21.4		78	0.117
	0.60	Damp	200	50		75	2	2.4	0.8	0.6	17.2	4.3	97	0.016
	0.60	Damp	200		50	0	0	2.5	0.7	0.5	20.1		83	0.086
	0.60	Damp	200		38	75	2	2.5	0.8	0.3‡ + 0.7§	18.1		92	0.045
Cupriferous U ore, Hite Mill feed	0.35	Damp	50		50	0	0	3.1	1.4	0.8	7.6		94	0.019
	0.35	Damp	50		50	0	0	3.9	0.6¶	0.8	7.8		92	0.023
Marysvale ore, VCA	0.20	Damp	160		24	38	1	11.9	5.2	0.7‡ + 1.1§	45.5		88	0.022

*Vol. % concentrated nitric acid in solvent.

†Based on assumption that 99 per cent of solvent and 90 per cent of total nitrate are recovered and that all CaO and H_2SO_4 are consumed.

‡$Ca(NO_3)_2$.

§Concentrated nitric acid.

¶Alcohol used in this test.

Table 5 summarizes some typical prior-sulfation tests on several carnotites and two Utah uranium ores, one from Marysvale and the other from Hite. The damp leaches are those in which the digestion was done at high per cent solids and in which the ores were not dried before being leached with mixed solvent. The dry leaches are those in which the sulfated pulps were dried before being leached with a single solvent, ethyl ether. The uranium extractions were generally quite good. The data on Indian Reservation carnotite ore show that when a larger amount of sulfuric acid is used the leaching is not as effective as when smaller amounts of sulfuric acid or lime are used. This inhibiting effect of excess sulfate has been observed in tests on other ores.[5,7,8]

DAMP VERSUS DRY LEACHING

The mixing and washing problem encountered when water is present in the pulp led to the use of mixed solvents in the so-called "damp leach." The use of a solvent like acetone for drying the pulp is a convenient laboratory method but poses the problem of water removal from the mixed solvent. Mixing and washing difficulties, however, may exist only when the leaching is done in the laboratory on a gram scale. In large-scale leaching operations there may be no problem at all. Testing of equipment suitable for mixing pasty pulps with a single solvent could be carried out on a small pilot-plant scale after consultation with process-equipment manufacturers. Time has not permitted such a study.

If a cheap, easy method of removing water from a barren mixed solvent can be worked out, the damp leach with mixed solvent would also appear to be feasible. No study of water removal methods has as yet been undertaken.

An alternative to damp leaching, either with mixed solvent or with a single solvent if suitable equipment is available, is to dry the feed material, whether raw, nitrated, or sulfated, before giving it a dry leach with a single solvent. The drying need not necessarily be complete but may be carried only to the point where the material is friable and crumbly enough to be mixed in a single solvent.

STATIC AND PERCOLATION LEACHING

Most of the laboratory lyometallurgical leach tests have been run in the apparatus shown in Fig. 3 and have been agitation type leaches. There has, however, been some work done on percolation and static leaching. In percolation leaching the solvent is percolated through a fixed bed of solid material. In static leaching the solvent merely contacts the solid without mixing or agitation of any kind during the leaching. Leach times in static leaching, where extraction depends exclusively on diffusion of ions or molecules through motionless liquid, are, of course, longer than times required for comparable results in agitation leaching where mixing aids diffusion. However, smaller quantities of solvent can be used in static leaching. Good extractions were obtained by static leaching from a number of materials, including the Marysvale ores and the cupriferous uranium ores from Hite, Utah.

Percolation leaching is used in hydrometallurgy to treat coarse materials that contain few slimes or ores from which slimes have been removed. The mechanical advantage of organic solvents over water is so great that adequate percolation rates can be achieved using only a foot or so of solvent head on beds of slimy materials up to a foot thick. Figure 4 is a graphical record of a percolation leach with nitric acid–ethyl ether solution (10 vol. % acid) on an 11-in. bed of −20-mesh Marysvale ore.[8] The average flow rate of solvent through the bed was 0.282 ml/hr/g of ore, or in more conventional units, 66.1 gal/sq ft/24 hr. Total percolation time was approximately 7 hr.

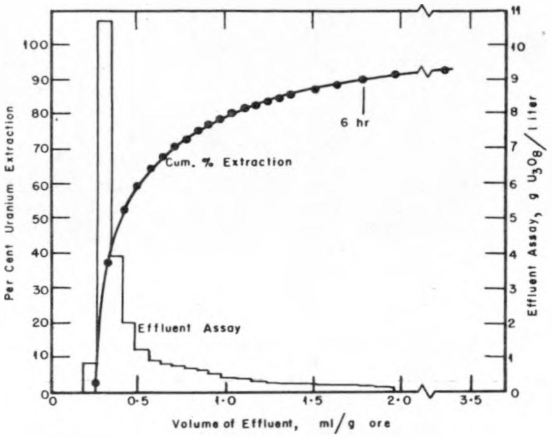


Fig. 4— Percolation leach of Marysvale ore with 10 vol. % nitric acid–ethyl ether solution. Charge, 150 g of −20-mesh ore; bed depth, 11 in.; average flow rate, 66.1 gal/sq ft/24 hr.

Included in Fig. 4 is the holdup liquor which was drained out of the bed at the end of the test. The final uranium extraction was as high as that obtained in the 1-hr agitation leach on the same material. Also, reagents were required in roughly the same amount in each test.

USE OF OTHER SOLVENTS

A few tests have been run on various materials using a solution of nitric acid in solvents other than ethyl ether, including acetone, isopropyl ether, ethyl acetate, hexone, and tributyl phosphate–kerosene solution.[4,5] Compared to ethyl ether, results were generally not so good, either in uranium extraction or in filterability of the pulp. The poorest filtration rates were obtained with the more viscous water-avid solvents, such as the tributyl phosphate–kerosene solution, although engineers of The Kellex Corporation[9] have found mixed solvent to give almost complete uranium extraction without filtration difficulty. A considerable amount of research work remains to be done on the problem of selecting the proper organic solvent to do a certain job.

An investigation has been started to test the ability of various solvents to leach an artificial mixture of nitrates of uranium and the impurities most frequently associated with uranium.[10] The nitrate mixture analyzed as follows:

U_3O_8	2.4%	Co	1.2%
CaO	2.8	Ni	1.2
Fe	8.2	Cu	1.2
Al_2O_3	11.0	MgO	0.8
Pb	2.3	Cr	0.8

Table 6 summarizes preliminary results of the survey. The extractions of elements or compounds other than U_3O_8 were generally determined by semiquantitative spectrographic analyses and hence are only rough approximations. Many solvents show good uranium extractions. The most selective leaching was done by some of the nitro compounds, particularly nitroethane. Further testing of these promising solvents will be undertaken on natural uranium ores. Notwithstanding selectivity considerations, however, it now seems that ethyl ether will rank close to the top of the list of solvents suitable for treating uranium ores when economic factors and over-all ease of handling are considered.

EXTRACTION OF OTHER ELEMENTS

Uranium ores and plant products frequently contain other valuable metals which can be extracted either with the uranium or in a subsequent step. Proper choice of solvent, other reagents, and pretreatment will determine whether or not a given element will be extracted. The by-product can either be extracted in a separate leach before or after selective uranium extraction or it can be extracted along with the uranium. By proper treatment of the pregnant solvent, separation of uranium from other values can be effected (see the section on "Production of High-purity Uranium"). Table 6 has considerable data concerning the extraction of elements other than uranium from an artificial ore. Presented below are data collected during test work on actual uranium plant products and raw materials.

DECLASSIFIED

Cobalt and Nickel

The precipitates obtained by the addition of lime (CX) and magnesia (MgX) to acid leach liquors from Congo pitchblende ores contain appreciable amounts of cobalt and nickel. When these materials are leached, either by the direct or the prior-nitration process using ethyl ether, uranium is extracted rather selectively. If acetone is used, however, cobalt and nickel are also extracted. Table 7 shows the results of a preliminary test in which this effect was observed. A sample of CX material was leached first with nitric acid–ethyl ether solution (10 vol. % acid) and then with plain acetone. The ether liquor and acetone liquor were separately stripped with ammonia gas, and the ignited precipitates were assayed for uranium, cobalt, and nickel. The cobalt and nickel appeared in the acetone solution. In other tests, where acetone and ether solutions were combined and stripped with ammonia, it was observed that the yellow uranium precipitate formed first, followed in order by the pink and then the green of cobalt and nickel. A fractional precipitation like this might form the basis of a method of separating these elements.

Table 6 — Leaching of Nitrate Mixture with Various Solvents

	Extraction, %									
Solvent*	U_3O_8	Ca	Fe	Al	Pb	Co	Ni	Mg	Cr	Cu
Diethyl ether	92	0.2	0.2	0.2	<0.1	10	10	3	<0.1	>20
Nitromethane	100	<0.1	0.2	<0.1	<0.1	10	10	3	<0.1	>20
Nitroethane	100	<0.1	<0.1	2	<0.1	<0.1	<0.1	3	<0.1	<0.1
1-Nitropropane	84	<0.1	15	<0.1	<0.1	<0.1	<0.1	3	2	<0.1
2-Nitropropane	100	<0.1	2	<0.1	<0.1	<0.1	<0.1	3	2	<0.1
Acetone	84	78.0†	4.0†	52.0†	15.0†	71†	92.0†	9†	3.0†	>20
Diethyl ketone	86	8†	0.2	<0.1	0.1	54†	35†	<1	<0.1	>20
Hexone	92	25†	0.2	2	<0.1	60†	40†	3	2	>20
Diisopropyl ketone	72	0.1	0.2	<0.1	<0.1	10	10	<1	<0.1	>20
Diisobutyl ketone	63	2	2	<0.1	<0.1	>20	>20	30	<0.1	>20
Methyl alcohol	82	>30	>30	>40	100	100	100	30	100	100
Ethyl alcohol	100	100	15	20	<0.1	>20	20	>50	>30	>20
n-Butyl alcohol	86	>30	15	>20	1	20	20	>50	>30	>20
n-Amyl alcohol	100	>30	15	20	<0.1	>20	>20	>50	>30	>20
Frother B-23	72	>30	2	2	<0.1	>20	>20	30	15	>20
n-Hexyl alcohol	99	>30	2	20	<0.1	100	100	>50	15	>20
Benzyl alcohol	50	>30	<0.1	20	<0.1	100	>20	30	2	>20
Acetic acid	73	>30	>30	>40	<0.1	>20	>20	>50	30	100
Propionic acid	96	15	15	20	<0.1	10	10	3	<0.1	>20
Ethyl acetate	100	>30	2	20	<0.1	100	>20	>30	10	100
Isopropyl acetate	52	2	2	0.2	<0.1	10	>20	>50	2	>20
Amyl acetate	82	19	2	2	<0.1	52†	40†	3	2	>20
n-Butyl *n*-butyrate	52	2	2	0.2	<0.1	10	>20	>50	2	>20
n-Butyl chloride	24	<0.1	0.2	<0.1	<0.1	<0.1	<0.1	1	<0.1	10

*Solvents contain 5 vol. % concentrated nitric acid (70 wt. % HNO_3).

†Chemical analyses. Unless otherwise indicated, all figures for extraction of elements other than uranium represent spectrographic approximations only. Uranium extractions determined by fluorimetric assay.

Copper

In the treatment of Congo precipitates some copper was also extracted. Copper did not precipitate from acetone upon ammonia addition but formed instead a blue complex. The copper present in ether solutions was found to precipitate with the uranium upon the addition of ammonia, but it was removed from the precipitate in the water wash as the soluble copper-ammonium complex.

The cupriferous uranium ores from Hite, Utah, averaged about 2 per cent copper. Copper extractions from those ores were poor by lyometallurgical leaching. However, the tests were designed primarily to recover uranium and not copper. By suitable modification of leaching conditions, copper could probably be recovered.

Vanadium

The lyometallurgical methods described have resulted in appreciably higher uranium extractions from carnotites than are now being obtained in practice. However, the vanadium extractions have been low.

Although vanadium recovery is not vital, it is a consideration. Treatment of sulfated carnotites by mixing with solid calcium chloride crystals either in lieu of or after calcium nitrate addition, followed by leaching with mixed solvent, gave vanadium recoveries of the order of 50 per cent, as good as present plant practice on low-vanadium carnotites.[7] Even if no nitrate at all is present in the system, uranium recoveries, although impaired, were as good as achieved in present operations, that is, over 85 per cent.

Table 7 — Direct Leaching* of CX Precipitate

	U_3O_8	Cu	Ni	Co
Head assay, %	31.0	0.48	1.24	1.58
Total extraction, %	98	68	67	77
Ether product assay, %	99†			
Acetone product assay, %	46		6	21

* Charge leached first for 15 min with 3.0 ml/g of 10 vol. % nitric acid–ether solution, displacement washed once with plain ether. Charge then releached for 5 min with 1.5 ml/g plain acetone, followed by one displacement wash of plain acetone.

†This product contained 91 per cent of the total uranium extracted.

RECOVERY OF URANIUM

The only uranium stripping method that has been studied is the direct ammonia precipitation of uranium from the pregnant solvent. Bubbling ammonia gas into the pregnant solution precipitates all the uranium and most other metallic ions present. Any free nitric acid is neutralized with the formation of ammonium nitrate. In the case of ethyl ether, when used alone, the ammonium nitrate precipitates with the uranium and can be washed out of the precipitate with plain water. In the presence of mixed solvents, part, if not all, of the nitrates remain in solution and could perhaps be recycled directly.

By washing the ammonia precipitate with water, water-soluble nitrates are removed, including water-soluble complexes such as the copper-ammonium complex. After ignition, the final purity of the uranium product depends on the raw material treated since, as shown in Table 6, ether will dissolve to a small extent certain nitrates other than uranyl nitrate. Product grades from leaching of low-grade ores have ranged from 70 to 90 per cent U_3O_8. Occasionally products assaying over 90 per cent U_3O_8 have been obtained.

PRODUCTION OF HIGH-PURITY URANIUM

Recent studies have shown that passing the pregnant solvent through a column of activated alumina before ammonia precipitation has considerably increased the grade of the final product. Assays exceeding 99.8 per cent U_3O_8 have been obtained.[6] The uranium passes readily through the column, and the impurities are rather strongly adsorbed by the alumina. This alumina purification is a typical chromatographic phenomenon, the yellow uranium band being the fastest moving of several colored bands. The column can be operated until the first impurity band breaks through.

The prospect of producing high-grade uranium directly from a low-grade ore, simply and at a relatively small cost, is particularly attractive since the product might be pure enough to by-pass present refineries. The idea of a chromatographic type purification process has not yet been evaluated. The British, however, have done some work of this nature.[11]

RECYCLING OF SOLVENT AND REAGENTS

By using a sealed system and condensers, it has been possible in the laboratory to recover over 99 per cent of the total solvent used. On a larger scale, losses could probably be reduced even further. The solvent may have to be treated to remove water, by rectification, by use of a dehydrating agent, or by a freezing process, before being recycled. If the feed material was dried or partly dried before leaching, water build-up in the solvent could be prevented. The study of solvent regeneration is one that remains to be examined in detail.

The nitrate used, added either as nitric acid or as a salt, can appear in several places: (1) the water wash of the ammonia precipitate, (2) the recycled barren solvent, (3) the water removed from the solvent in the regenerating step, or (4) the leach residue. Nitrate appearing in the directly recycled barren solvent probably will be usable without collection and conversion to calcium nitrate or nitric acid. The nitrate appearing in the water solution, either from de-

DECLASSIFIED

hydration of the solvent or from water wash of the precipitate, can first be treated with lime to evolve ammonia. It has not been determined whether or not it would be economic to recover this ammonia for reuse. The remaining calcium nitrate solution can be evaporated to dryness and the salt can be reused as such, or, by further heating, the calcium nitrate can be decomposed to regenerate lime and nitric acid. When treating low-grade ores by direct leaching or prior sulfation, it almost always will be unprofitable to recover the small amount of nitrate in the tails since the quantity of solid to be heated is so large.

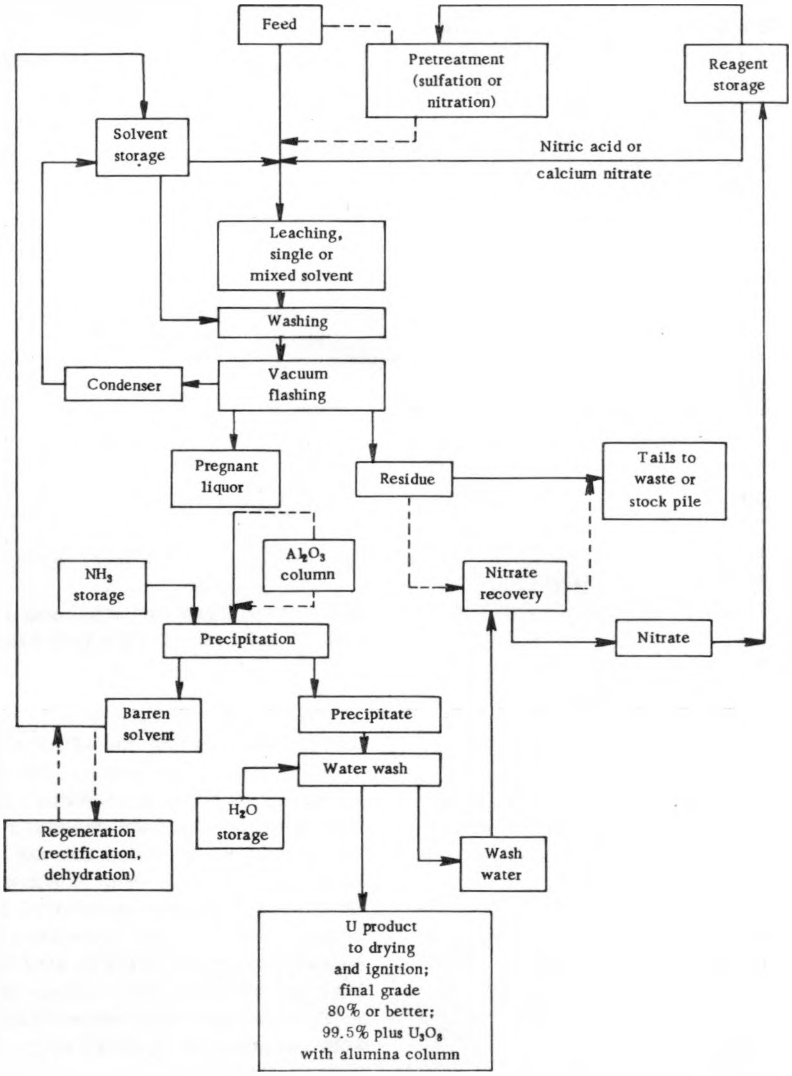


Fig. 5—Schematic flow sheet for lyometallurgical leaching of uranium-bearing materials.

The study of nitrate economy is another subject that requires detailed study at the pilot-plant stage.

OVER-ALL PROCESS AND COST ESTIMATES

Figure 5 is a more complete flow sheet than those of Figs. 1 and 2, and it shows various steps in the three lyometallurgical processes suitable for treating uranium-bearing materials. Almost all the low-grade domestic uranium ores that have been tested are amenable to either direct leaching or leaching after sulfuric acid digestion. Leaching after nitric acid digestion does not appear so attractive as the other two methods for treating low-grade western ores.

Some preliminary calculations have been made to determine approximately what it would cost to treat low-grade western ores by the prior-sulfation method using static digestion at high per cent solids and mixed solvent for leaching. Reagent consumptions were assumed to be 1 per cent of solvent used, 10 per cent of the nitrate added, and 100 per cent of the sulfuric acid and ammonia. An average recovery of 90 per cent of the total uranium was assumed at all grades of ore. The lyometallurgical plant was planned to treat 5 tons of ore per hour, or 120 tons/day for 300 days a year. Reliable equipment costs were obtained from manufacturers or from recent literature, and it was assumed that the solvent would be dehydrated by rectification in a bubble-plate tower. The total installed-equipment cost amounted to approximately $529,600. After adding additional amounts for engineering and construction (25 per cent), a size factor (15 per cent), and a contingency allowance (30 per cent), the total indicated capital investment was $900,000.

In determining the cost per pound of U_3O_8 extracted, estimates were made of (1) direct costs, including operating labor, supervision, record keeping, analysis, plant maintenance, operating supplies, payroll overhead, power and reagents; (2) fixed costs, including taxes, insurance, interest, depreciation and amortization (investment written off in 10 yr); (3) indirect costs or burden, including 50 per cent of each of the labor, supervision, record-keeping, analysis, plant-maintenance, and operating-supply costs; and (4) a contingency of 15 per cent on (1), and 10 per cent on (2) and (3). Based on percentages these figures turned out to be: direct costs, 60.6 per cent; fixed costs, 17.4 per cent; indirect costs, 10.2 per cent; and contingencies, 11.8 per cent of the total cost. Results of these preliminary cost calculations are presented graphically in Fig. 6 where the estimated cost per pound of uranium extracted is plotted against the grade of ore treated.[12]

A treatment cost of $12.70 per pound of U_3O_8 extracted from 0.1 per cent U_3O_8 ore seems reasonable enough considering present costs of treating carnotites on the Colorado Plateau. The treatment cost drops to $6.40 per pound of U_3O_8 with a rise in grade of ore to 0.2 per cent U_3O_8.

SUMMARY

The lyometallurgical process was conceived and has been used mainly for treating uranium ores. Because of the solubility characteristics of uranyl nitrate most of the test work has been done with ethyl ether and nitric acid. Since studies of solution chemistry have been almost wholly concerned with water and very little is known about the solubility of various salts in organic solvents, lyometallurgy is a nearly virgin field. We now have only the barest idea of what solvent and what inorganic reagent can be used to give the most selective and complete extraction of various ore constituents.

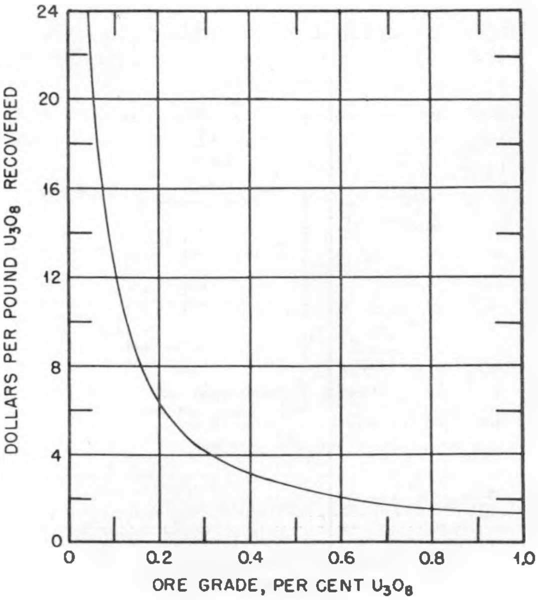


Fig. 6—Estimated cost of treating low-grade western uranium ore by prior-sulfation lyometallurgy process.

Most of the laboratory work to date has been concerned with testing the efficacy of lyometallurgical leaching on a large number of uranium-bearing raw materials and plant products. Consequently a good deal of study has been devoted to the matter of pretreatment and leaching, but not too much effort has been spent on the study of solvent stripping, regeneration, and reagent recovery. Results of lyometallurgical investigation have shown that the method is an attractive alternative to acid leaching for beneficiation of uranium ores. Some pertinent topics and questions concerning lyometallurgy which still remain to be investigated in detail are:

Mechanical considerations

1. Equipment design for damp leaching and dry leaching
2. Size reduction of feed; to what extent is it required
3. Equipment for sulfation at high per cent solids
4. Equipment design for static, percolation, countercurrent, and cyclic leaching
5. Equipment for nitration

DECLASSIFIED

Selection of solvent

1. Further search for useful selective solvents, using systematic approach on synthetic feeds
2. Testing of solvents shown in Table 6, plus others, on raw materials
3. Use of diluents
4. Combinations for mixed-solvent leaching

Recovery and recycling of solvent and reagents

1. Methods of water removal from barren solvent; whether or not required
2. Recovery of solvent from pasty, damp pulps
3. Decreasing solvent loss below 1 per cent in large-scale operations
4. Where does nitrate finally appear, and how is it best recovered
5. Can nitrate by recycled as ammonium nitrate in barren solvent
6. Economics of ammonia recovery

Extension of process to other metals and minerals

1. Suitable solvents, acids, and other reagents for specific metals
2. Survey of various ore minerals

Other methods for uranium extraction

1. Pretreatment with acids other than nitric and sulfuric, or with bases rather than acids
2. Other methods of nitration and sulfation (NO_2 or SO_3 gas)
3. Use of other acids in solvent besides nitric

Economic evaluation

1. Upgrade scale of testing to pilot-plant size
2. Substantiate and revise cost estimates already calculated

REFERENCES

1. A. M. Gaudin, R. Schuhmann, Jr., J. Dasher, R. D. Macdonald, D. Kaufman, J. H. Pannell, and D. R. George, The Recovery of Uranium from Low-grade Ores, (Report MITG-243), J. Met. Ceram., 5: 38 (June 1950).
2. A. M. Gaudin, J. Dasher, David Kaufman, Sara E. Bailey, and N. H. Schiff, Production of a High-grade Uranium Precipitate from Ore Leach Solutions, (Report MITG-254), Reactor Sci. Technol., 1: 82 (April 1951).
3. Paul Galvanek, Jr., and David Kaufman, Application of the Solvent Leaching Process for the Concentration of Uranium from Rand Ores, Report MITG-A79, Nov. 15, 1949.
4. Paul Galvanek, Jr., and David Kaufman, Further Studies on Solvent Leaching — Uranium Recovery from Eldorado Concentrate, Congo Precipitate, Rand Precipitate, and Carnotites, Report MITG-225, Mar. 20, 1950.
5. F. W. Bloecher, Jr., Lyometallurgy Survey, Report MITG-247, Jan. 25, 1951.
6. Paul Galvanek, Jr., Application of the Solvent Leaching Process for the Concentration of Uranium from Sunshine Ores, Report MITG-232, Mar. 20, 1950.
7. Paul Galvanek, Jr., Lyometallurgical Treatment of Sulfated Carnotites and Other Ores, Report MITG-246, Feb. 15, 1951.
8. F. W. Bloecher, Jr., Lyometallurgical Tests on Marysvale Uranium Ores, Report MITG-252, Nov. 30, 1950.
9. The Kellex Corporation, Progress Reports for March through July, 1950, Reports KLX-1201 to 1205.
10. William V. Ward, A Search for Selective Solvents of Uranium Nitrate from Other Nitrates, Report MITG-244, Jan. 17, 1951.
11. W. Ryan, The Preparation of High-purity U_3O_8 by Solvent Extraction in Combination with Solid Adsorbents, Report CRL-AE-43, November 1949.
12. F. W. Bloecher, Jr., Estimated Costs of Treating Western Ores by Lyometallurgical Leaching, Report MITG-265, Feb. 28, 1951.

January 1951

DECLASSIFIED

TID-2502(Del)

THE HOT LABORATORY AT BROOKHAVEN NATIONAL LABORATORY

By W. E. WINSCHE, L. G. STANG, JR.,
GERALD STRICKLAND, P. RICHARDS,
G. J. SELVIN, F. HORN, and G. BENNETT

Reactor Science and Engineering Department
Brookhaven National Laboratory

Report TID-5020

ABSTRACT

The hot laboratory at Brookhaven National Laboratory has been specifically designed and built to handle and process multicurie amounts of radioactive materials. It is operated by a permanent staff in such a way that others can also use the various facilities required for this type of work. A wide variety of facilities is available, and use is already being made of them as indicated by the scope of the research and operations program presently under way. The general philosophy used in designing the building is outlined and the facilities themselves are described in detail.

INTRODUCTION

Early in the planning stages of Brookhaven National Laboratory the need was felt for a building specifically designed to handle and process multicurie amounts of radioactive materials, a building which would be stocked and maintained by a permanent staff and could be used by others when they had occasion to handle anything from a few millicuries to hundreds of curies of activity. The hot laboratory described in this article represents the fulfillment of this need. Some of the special facilities of the building will be of particular interest because of their radical departure from convention.

The building was occupied by the permanent staff in the summer of 1950. Already some special handling devices have been built for particular jobs, and it is expected that in time a stock of such items as tongs, manipulators, dry boxes, equipment racks, and special valves will be built up so that the proper piece of equipment for any particular job will be on hand. By now also most of the special features have been put to actual use.

RESEARCH AND OPERATIONS PROGRAM

The building is designed for a wide variety of operations, as will be seen from some of the activities presently going on in it. The resident building staff operates and maintains the building as a specialized research laboratory. In addition to the ordinary duties encountered in an operation of this sort, the staff performs such special functions as (1) monitoring the building ventilation exhaust to detect, and thereby check the spread of, air-borne contamination, (2) monitoring and treating all liquid waste generated within the building and most of that discharged from the reactor building, as well as all the radioactive waste generated at other buildings on the site, and (3) advising and assisting visitors in setting up the proper experimental equipment. It is planned to add an analytical service section in the near future to perform the many radiochemical analyses required in processing radioactive material.

Two projects of general interest were undertaken by members of the Hot Laboratory Group, and these are now nearly completed. The first is a generator to

/

DECLASSIFIED

make 2.4-hr I^{132} available for general research. The development of this generator is described in the March 1951 issue of "Nucleonics." The second project is the development and construction of a closed-cycle dissolver. Uranium dissolved within a few hours after irradiation is very active with short-lived volatile isotopes of xenon, krypton, bromine, and iodine. The dissolving of even moderate amounts of uranium with release of these activities to the atmosphere would exceed acceptable tolerance levels. In order to do research and development with fresh uranium, a control and storage system was developed.

The Extractive Distillation Group has installed equipment for relative volatility measurements in the systems of MoF_6, TeF_6, UF_6, and BrF_3. In addition, equipment to test the corrosion resistance of aluminum alloys, welds, nickel-aluminum couples, etc., is in operation. This group has under construction several 3- to 4-in.-diameter columns and associated tankage for pilot-plant testing of the efficiency of separation of TeF_6, UF_6, and BrF_3. This work is being done in cooperation with similar work by J. J. Katz at the Argonne Laboratory.

The Waste Concentration Group has under test an 80 gal/hr compression-distillation evaporator manufactured by the Cleaver-Brooks Co. This unit was modified to include the fiberglass deentrainment unit developed at BNL. Operating characteristics and decontamination ability have been tested, and studies on scaling with general laboratory waste liquids have just been started. The work of this group is now changing over to the evaluation of waste utilization. Several kilocurie sources of tantalum and cobalt are now in the Brookhaven reactor, and preliminary studies on the shielding and handling of these sources will be conducted in one of the semihot laboratories described below.

The Metallurgy Division has been measuring the changes in the physical properties of invar which result from neutron irradiation. This work has been on an interim basis in a semihot laboratory. For general testing (stress-strain, hardness, impact, etc.) of radiation damage of reactor materials, more permanent facilities will be needed. Detailed designing will be started soon on a series of shielded cubicles. Each cubicle will be specifically designed to permit standard metallurgical testing by remote control.

The Fuel Processing Group has been measuring the distribution coefficient of rare earth metal and uranium between molten bismuth and the fused eutectic of LiCl and KCl. Experimentation thus far has been on a laboratory scale since larger scale tests with irradiated uranium require the use of a semihot laboratory.

The Medical Department is using an 80-curie cobalt source to irradiate small animals and chicken embryos. The individual sources are arranged in a grid to give a fairly uniform field of ~1000 r/hr. The grid is mounted on slides so that the sources can be moved into a shield cave while the apparatus for the experiments is being set up and dismounted.

A group from the Physics Department is preparing to work with 1 or 2 curies of tritium, and members of the Health Physics Division have used the hot laboratory facilities to load a lead pig with 200 curies of Co^{60}.

GENERAL PLAN

Philosophy

The strict control of contamination was axiomatic in the design and operation of the hot laboratory. This is exemplified by the fact that all exhaust air from areas where radioactive material is used is in every case filtered through a CWS 6* filter and in some cases is also scrubbed, monitored for activity, and exhausted through a 325-ft stack. No liquid wastes are released from the laboratory which contain more than 3×10^{-11} curies/ml, and for a three-month average this figure must not exceed 3×10^{-12} curies/ml. Not more than 1.5 curies of liquid waste may be released in any 1 yr. All other liquid wastes are stored indefinitely. Contamination is further controlled by the general practice of using closed systems for chemical processing; such techniques as pouring radioactive liquids from open beakers and flasks are strictly avoided.

Thicknesses of shielding walls in general were calculated to attenuate a beam of 2-mev γ rays to a radiation level of 6½ mr/hr.

To facilitate the handling and storage of wastes, they are divided at the source into one of the five following types depending on their content:

A. Wastes containing accountable material
B. Wastes of high specific activity which do not contain accountable materials
C. Wastes high in chlorides or solvents
D. Wastes of low specific activity
F. Strictly cold wastes.

All these types are monitored.

Layout

The location of the hot laboratory with respect to the reactor building, the fan house, and the stack is shown in the aerial view, Fig. 1. Figure 2 shows a plan view. With the exception of the Health Physics office, which is located in the working area on the main floor, all other building offices are located on

---

*A paper filter of exceptionally high efficiency, developed and manufactured by the Chemical Warfare Service, now the Chemical Corps of U. S. Army.

the ground floor, well removed from any possible contamination.

In general, the main floor plan is arranged so that the rooms which should be, or will be, the "coldest" or "cleanest" are farthest to the east, i.e., farthest removed from the hot area. Thus the personnel lockers, the physical-measurements laboratory, and the counting room, in which there should be no loose activity, are all at the east end of the building, whereas the equipment-repair room to which contaminated equipment will be taken for repair is adjacent to the hot area. In this way it is hoped to eliminate or at least minimize any cross contamination of areas.

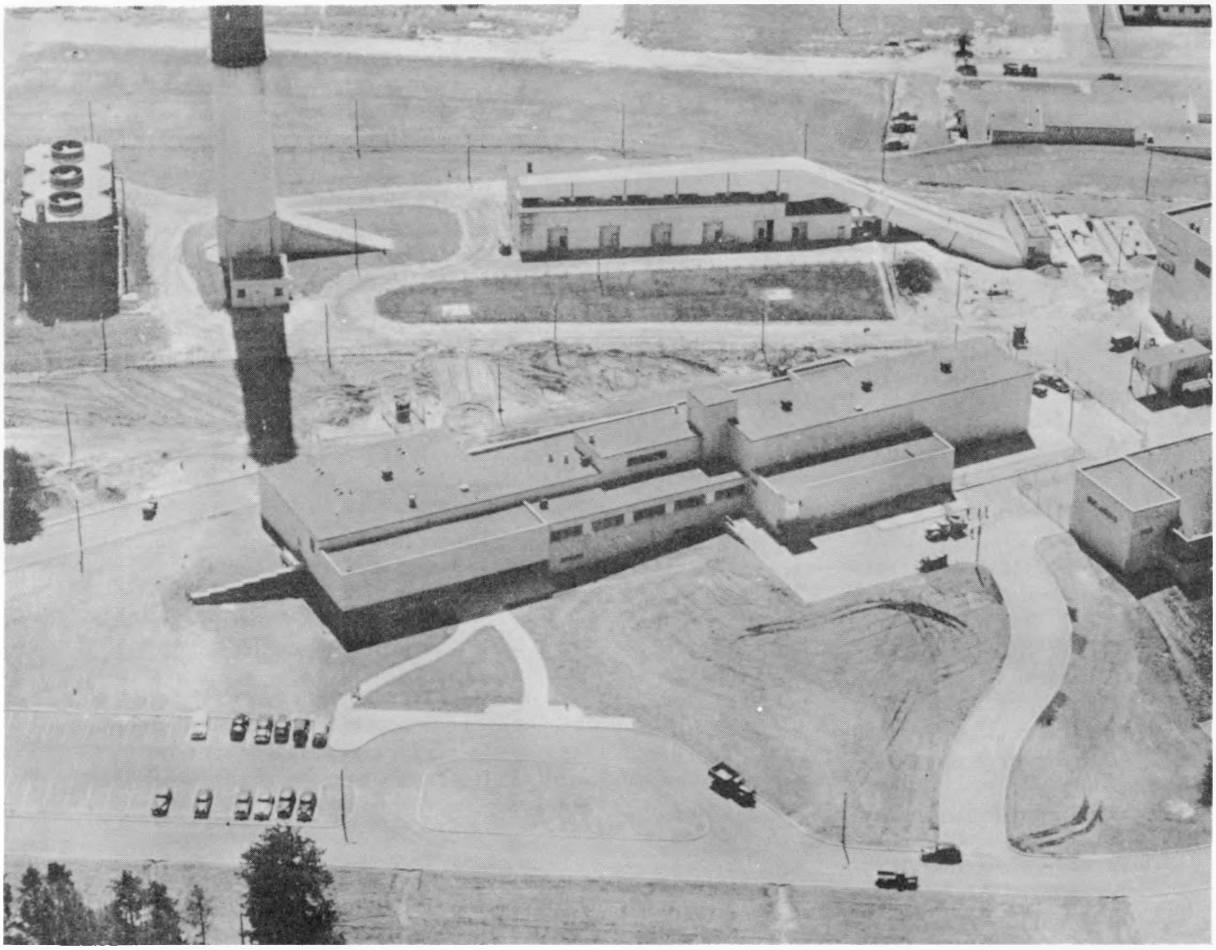


Fig. 1—Aerial view showing hot laboratory, reactor building with laboratory wings, stack, and fan houses.

As will be seen later, one of the chief advantages to the Brookhaven type of hot cell is the ability to build equipment out in the open and later to place it in the hot cell. The equipment-assembly room is provided as a place for the construction of equipment. A machine shop, a glassblowing shop, and the equipment-repair room are, for convenience, all located adjacent to the equipment-assembly room.

It will be noted that one double locker room is provided for men and another for women. In the event that the building should ever become contaminated to the point where it would be necessary for personnel to change clothes when going to and from the main floor, one locker room will be used for street clothes and the other duplicate locker room will be used for protective clothing. A shower room connects the two. At present the use of a lab coat is optional in the cold area and mandatory in the hot area. Personnel are not required to change clothes or shoes in going to or

3

DECLASSIFIED

from the main floor, and the use of the showers is optional. They are, however, required to monitor themselves at "sufficiently frequent intervals to ensure that they are free of contamination."

The building was designed to accommodate a total of approximately 80 men and 10 women, including both technical and supporting personnel and transients, i.e., people who use the facilities for only a few days or weeks at a time. The total usable floor space is of the order of 33,000 sq ft, broken down as follows:

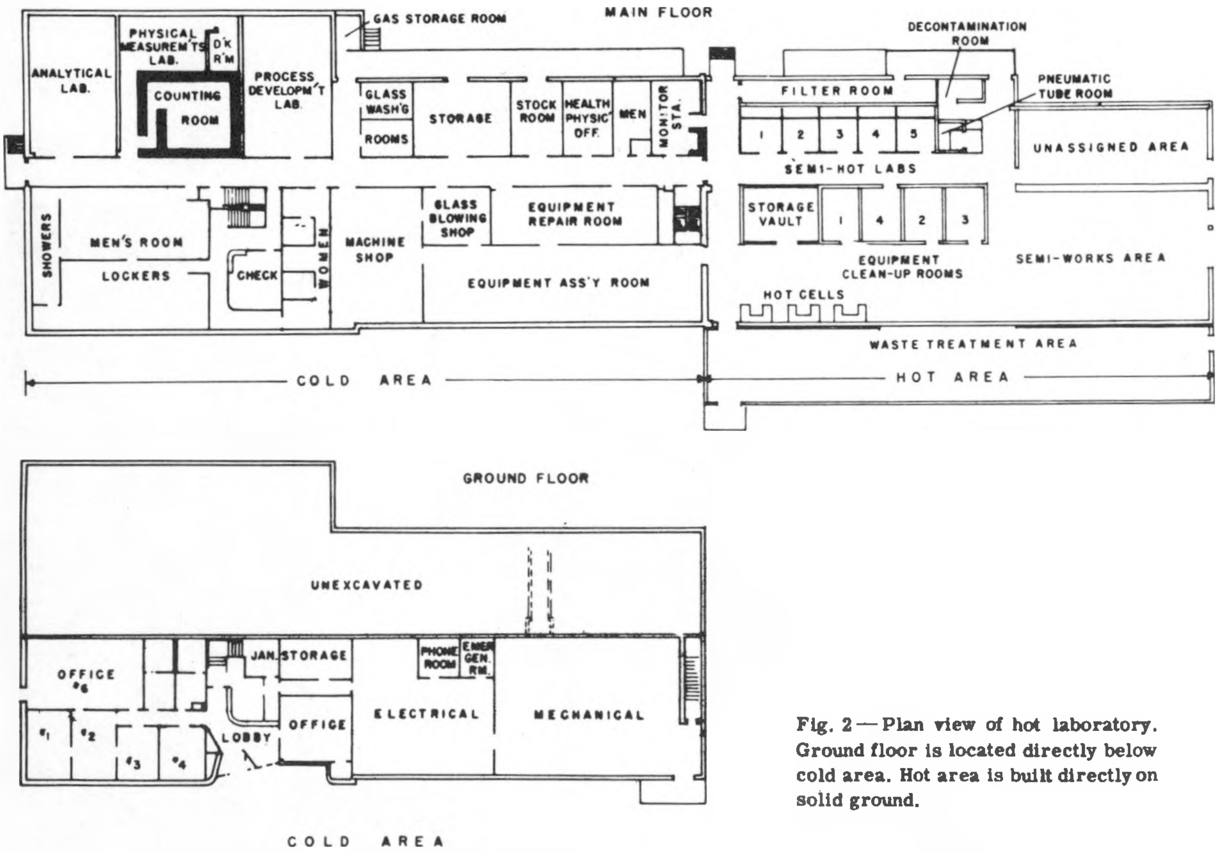


Fig. 2 — Plan view of hot laboratory. Ground floor is located directly below cold area. Hot area is built directly on solid ground.

Cold area, ground floor	7,000
Cold area, main floor	14,000
Cold area, attic	1,000
Hot area, main floor	11,000
Total	33,000

In laying out the plan of the building, the main emphasis was placed on the proper grouping of the areas in accordance with their function and the activity level or radiation level expected in each. To achieve this result and at the same time provide a building which could later be expanded considerably would have resulted in a considerable increase in cost according to the contractor, The H. K. Ferguson Co. Therefore, in order to keep the construction cost to a minimum, the plans allowed only limited room for future external expansion, such as an additional analytical laboratory on the east. The present building provides space for five more laboratories similar to the existing semihot laboratories (see "unassigned area" Fig. 2), and foundations exist for the addition of three more hot cells just west of the present three.

Ventilation Pattern

The entire main floor is under forced ventilation, and in addition the hot area, analytical laboratory, physical-measurements laboratory, counting room, and process-development laboratory are air conditioned. In general, the pattern of air flow is always from a cold area to a warmer one, speaking in terms of potential contamination. No air is recirculated. All supply air is filtered as it enters the building to remove gross dust. All exhaust air from areas in which radioactive material may be present is filtered through a CWS 6 filter. Air from rooms such as the

118
4

DECLASSIFIED

machine shop and the glassblowing shop, where there should be no radioactivity, is blown directly out onto the roof without filtering.

A small difference in air pressure is maintained between the cold area and the hot area so that when a connecting door is opened the air flow is always from the cold area to the hot area. This is accomplished by means of a controller mounted on the common wall. When the pressure difference becomes too small this controller actuates roof exhaust fans in the hot area.

Equipment in the hot area can be vented through pipes which lead to a caustic scrubbing tower to remove contaminants such as iodine. This procedure will be described below.

SPECIAL FACILITIES

Hot Cells

Three hot cells are provided. These are rooms 4 ft wide, 3 ft deep, and 8 ft high, surrounded on the sides, rear, and top by 3 ft of ordinary concrete. Two of these rooms are shown in Fig. 3. The opening in the front is closed by two solid-steel doors 1 ft thick, 11 ft high, and weighing 11 tons each. The doors roll sideways and are hydraulically actuated. The cells were designed to handle 50 curies of a 2-mev γ emitting material, and they can accomodate proportionately larger amounts of lower energy isotopes.

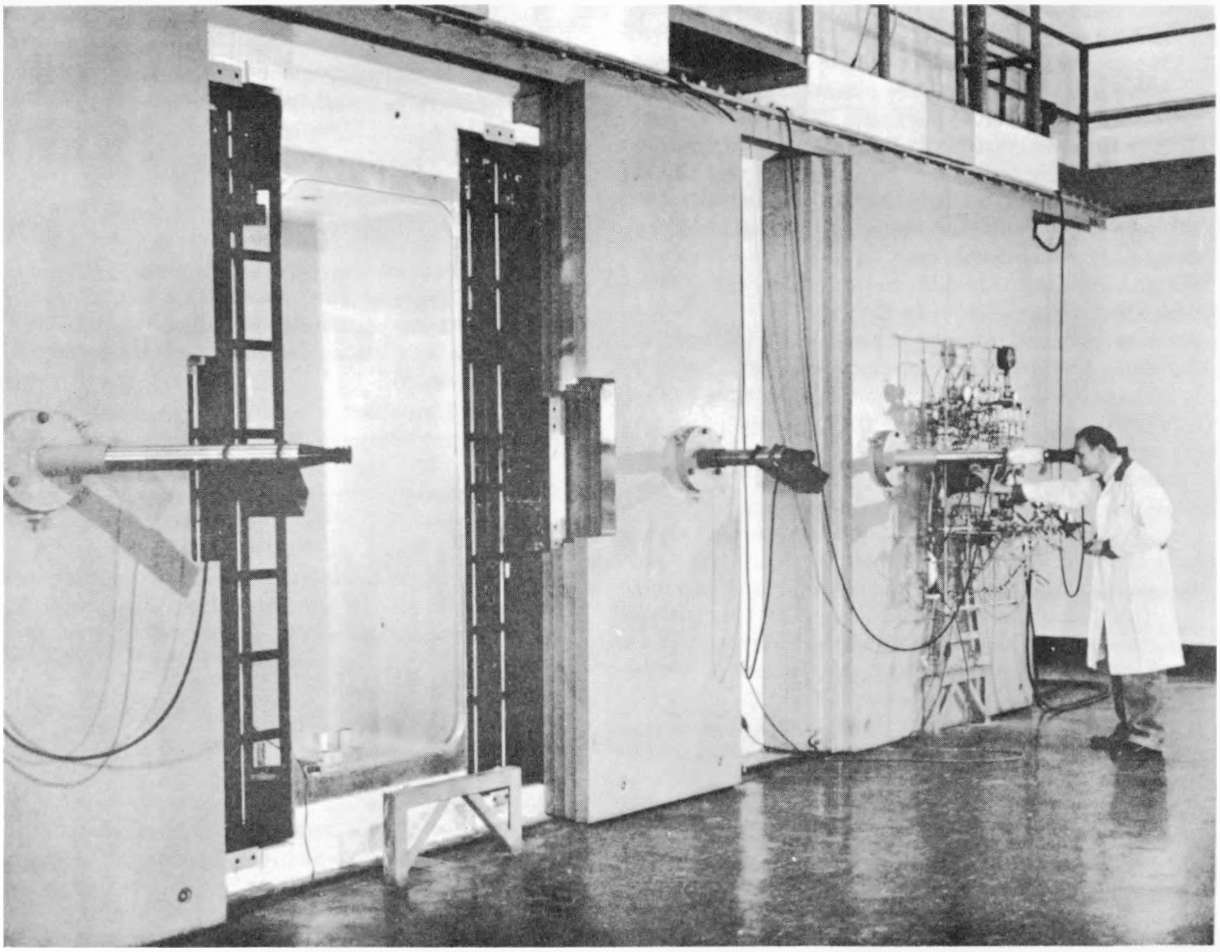


Fig. 3—View of two of the three hot cells. Picture shows hot cell on right with doors closed, equipment in place, and operating control panel exposed. Hot cell on left has doors open showing interior of cell.

714 119
5
DECLASSIFIED

As can be seen from Fig. 3, the doors have stepped edges which mesh together when they are closed to eliminate the straight-line penetration of radiation. Also seen in Fig. 3 is a rectangular opening in the doors for the insertion of a special plug or hub around which fits the apparatus to be used in the cell. The plug is mounted on a stand and is perforated by many tubes, some spiral and some straight. On either side of the plug there is a pipe rack, one for the remotely operated equipment and the other for all the controls. Connections between the two racks are made through the tubes in the plug.

This type of setup permits all the equipment to be assembled and tested in the equipment-assembly room rather than in the actual hot cell. The equipment can be put through a series of dummy runs using cold chemicals and/or tracers. Only after this equipment is thoroughly tested and checked is it placed in the hot cell. The latter operation is accomplished by picking up the entire assembly as a unit on a fork lift truck and placing it in a hot cell. The doors are then closed around the central block.

A stainless steel diaphragm mounted on the central block fits just inside the doors. Around the edge of this diaphragm is a large Tygon tube which, when inflated, seals the diaphragm to the cell and prevents any contaminated liquid or vapor from leaking out the front wall in case of an accident inside.

When an experimental run is completed the equipment is rinsed out internally and sprayed down externally to remove the gross activity. After it has dried, the doors are opened, and it is removed and placed in one of the equipment-clean-up rooms for further decontamination as necessary. Both the overhead crane and the lift truck used in moving the equipment can be operated remotely from a distance of 20 ft.

The advantages to this type of design and operation are manifold. The most significant of these is the fact that the hot cell is tied up only during the actual hot run, that is, both the assembly and the decontamination are done in rooms separate from the hot cell. Not only does this result in increased hot-cell efficiency but it makes for easier working conditions because, when the equipment is being worked on, it is out in the open where there is easy access to all sides of it. Also important is the fact that different apparatus can be used consecutively in the same cell without having to tear down the first to make way for the second. For instance, suppose a setup for separating isotope A is in current use in the cell and suppose that it is desired to produce, for a short period of time, isotope B, which requires an entirely different apparatus. Apparatus A can be removed and apparatus B can be inserted. When isotope B has been separated, that apparatus can be removed and the original apparatus for use with isotope A reinserted. Such flexibility of operation is difficult to achieve in hot cells where the equipment must be assembled inside the cell.

Hot-cell Periscopes

Since, among other reasons, the hot cells are designed to accommodate a variety of equipment (including glass vessels), it was felt necessary to incorporate some sort of optical viewing equipment.

During the early design stages of the hot-cell structure, G. S. Monk of the University of Chicago was approached with the problem of providing improved viewing instruments for the cell. The design used for other cells already in existence produces a view which is always reversed and is more often oblique than erect. In this case a design was desired that would result in a convenient and realistic view of the cell interior.

The design developed by Monk provides the observer with a view which is erect, unreversed, and brought to focus in an eyepiece conveniently fixed with respect to a process panel board. Only two periscopes are required for each cell, instead of possibly three or four, and two observers can use them simultaneously (see Fig. 4).

The view provided is equivalent to that seen by a person looking horizontally into the cell from a front corner (left or right) at a particular elevation. If it were possible to locate the eye and scan at any elevation along a front cell corner, the capabilities of the instrument would be duplicated. The instrument has a field of 25 deg at approximately unity magnification, and it is possible by moving a knob to increase the magnification with a corresponding reduction of field. The use of two periscopes for each cell results in a more practical observation system since greater coverage is provided, two views of a given object are possible, and a factor of safety in event of failure is acquired.

Specifications for the instrument were written, and a contract was made with Baird Associates of Cambridge, Mass., for further development of the design and for construction of a full-scale working model. This model was satisfactory and performed as prescribed. However, the Thorne-Brown Co. of Westport, Conn., improved the design and built the six periscopes used in the present three hot cells. In general, their system is easier to operate, has improved actuating mechanisms, and is more versatile; it also contains one, rather than two, traveling optical assemblies.

The complete periscope consists of an elevator housing assembly, telescope tube assembly, control box, and all necessary electrical components. Figure 5 shows a right-hand housing assembly, with the cover plates removed, and a left-hand telescope tube, with its control box. The left-hand edge of the housing

DECLASSIFIED

serves as a sealing surface for the inflatable tube carried on the diaphragm which covers the cell opening. The force exerted by this tube is transmitted to the steel shielding insert (A) which supports the housing by thrust girders (B). The housing is also gasketed to the hot cell liner and contains long narrow windows oriented at 45 deg to the cell corner.

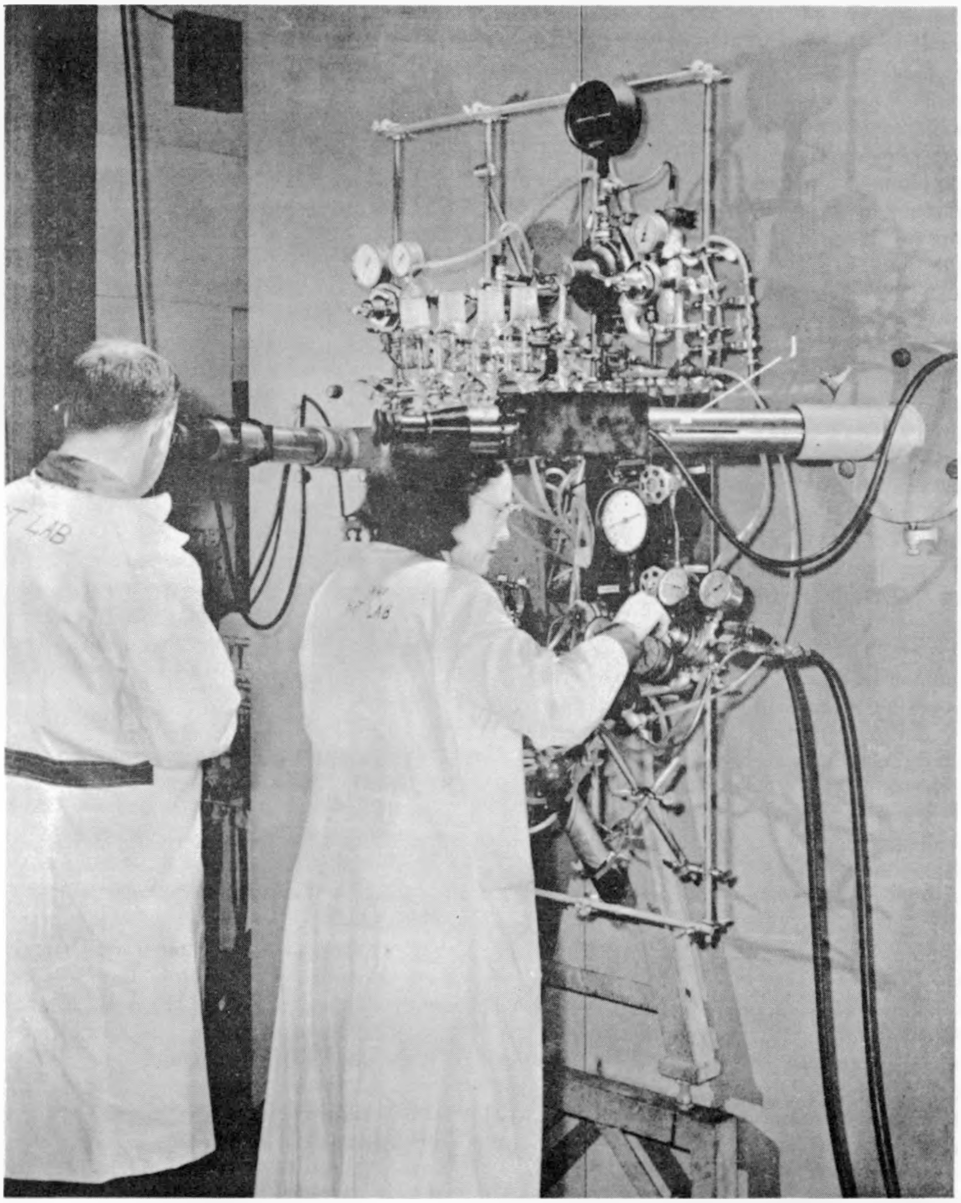


Fig. 4—Close-up of control panel at hot cell 1, showing doors closed and equipment in operation.

Each periscope is composed of three separate optical subassemblies, two of which are linked to the third only when the steel doors are closed. The housing unit contains a horizontal elevator tube (C) which is carried on guide rods (D) and is driven up and down by means of a small universal motor (E), ladder chain (F), and counterweight (G). The end of the tube facing

DECLASSIFIED

the cell interior carries a scanning head, reversing prism, and objective lens, and the opposite end carries a first erector lens, stationary prism, and flip-over prism. Fixed to the rear of the housing is a flip-over mirror (H) which links the above optical assembly to the telescope tube carried by the door. The flip-over mirror and prism are mechanically shifted to their proper positions by detents as the elevator tubes passes the mirror, and it is here that the system has an inherent blind spot; however, the field of view is such that each instrument covers the blind spot of the other. The telescope tube contains three

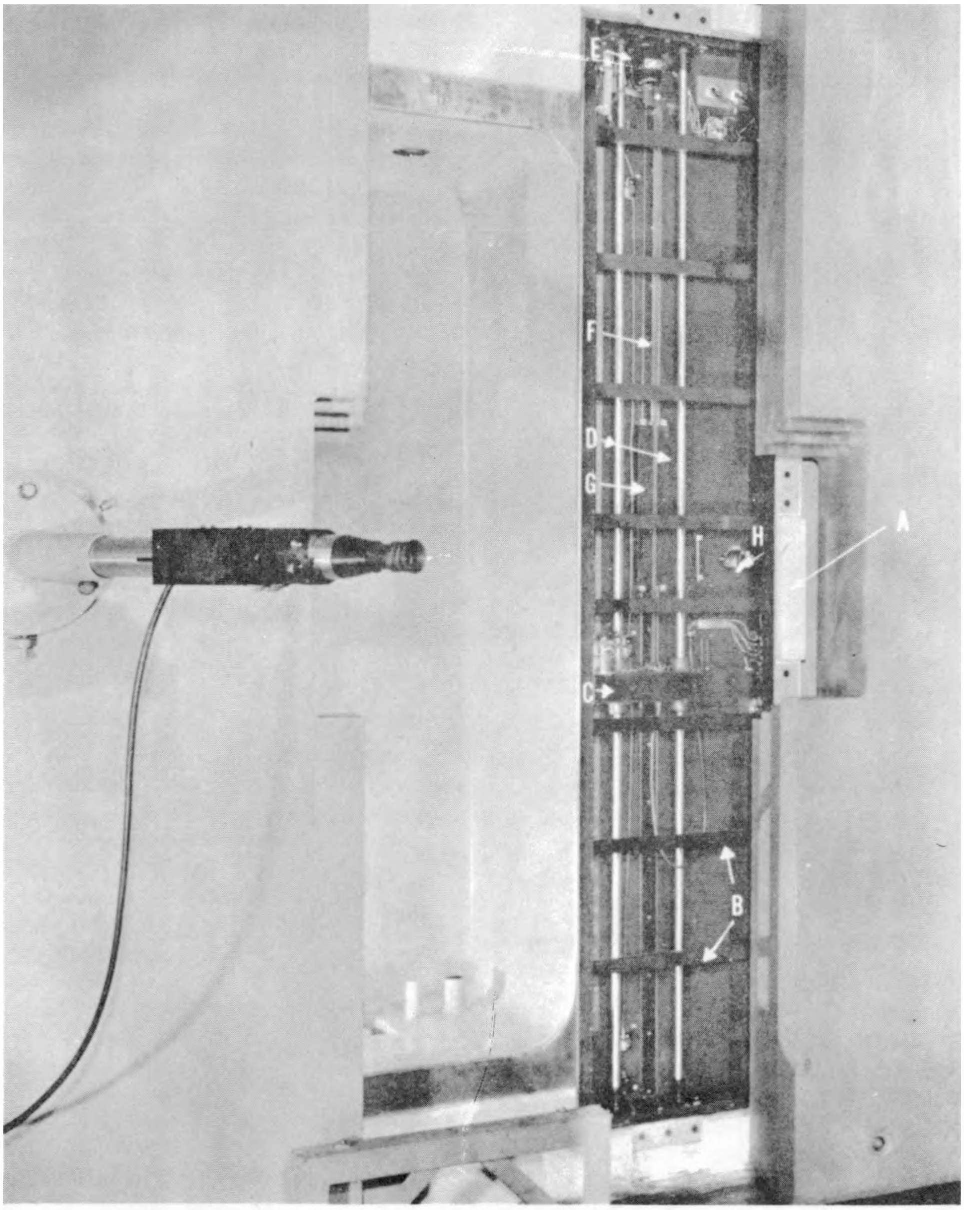


Fig. 5—View of a hot cell with left door in operating position and right door rolled back to show periscope mechanism. Cover plates have been removed to show interior of periscope.

DECLASSIFIED

second erector lenses and an eyepiece. The stationary prism prerotates the image through the 60-deg angle at which the telescope tube is set in the door.

The 25-deg field of view of the instrument is reduced to about 15 deg at the top and bottom of the cell. This reduction of field was accepted because the necessary optical components were readily available and because scanning can partially offset the loss. The variable magnification or "zoom" feature of the system is achieved by moving as a unit the pair of erector lenses closest to the eyepiece. This feature was incorporated by the Thorne-Brown Co. and has a magnification ratio of 2. When the zoom control (Fig. 4, J) is at mid-position, the erector lenses are located as in the original design and the field of view is 25 deg. Refocusing of the eyepiece is not necessary if the control is moved from one extreme to the other. The depth of field is such that refocusing of the eyepiece is necessary only for objects less than about 12 in. from the scanning prism.

The scanning prism is controlled by a pair of Selsyn motors (K), and it is the shaft of the motor located in the control box that is used to govern the scanning and elevating motions. Rotation of the control knob causes the prism to scan to the right or left, and an upward or downward motion of the knob raises or lowers the elevator tube.

Microswitches add resistance to the motor circuit at the extremes of the system to decelerate the elevator tube, and a second pair limit its travel. Resistance is also automatically added to the circuit to decelerate the tube as the prism and mirror are turned to their new positions. The weight used to counterbalance the elevator tube actuates all five switches.

Numerous minor modifications have been made in the instruments since they were installed, and other improvements may be made in order to eliminate sources of failure. In actual operation the periscopes have readily provided the improved viewing conditions originally desired.

Semiworks Area

The semiworks portion of the hot area is used for work of an intermediate engineering scale as contrasted with the work that can be performed in the hot cells. It covers a volume 36 ft wide, 56 ft long, and 25 ft high, and has an 8-ft-wide central corridor which divides it longitudinally. Each half is subdivided into four 14- by 14-ft areas called "work stations," each of which has its own mechanical, ventilating, and waste-disposal facilities. Some work will undoubtedly require the use of more than one station since it is difficult to predict the size of a work area suitable for many types of experiments. All equipment will be surrounded by the amount of shielding material required rather than by a standard size or type of shield. The floor is designed to carry a uniform loading of 750 lb/sq ft (nominal rating), and it can carry much greater loads locally if adjacent areas are not loaded fully.

Heavy equipment can be handled by the 3-ton overhead crane which serves the entire hot area. Equipment which is less than 8½ ft high can be transferred to the monorail for transport to the decontamination cell or for loading on a truck at the hot loading platform. A 12- by 12-ft roll-up door at the west end of the semiworks area can be used for other outside handling operations.

Figure 6 shows the facilities available at a typical work station. Beginning at the left, three types of alternating current electrical service are available: 220 volt, 3 phase; 220 volt, single phase; and 110 volt with additional emergency service. Emerging from the sheet metal dust cover against the wall are vacuum, 100 psi air, 100 psi steam, 15 psi steam, gas, and cold water lines. The stainless steel ventilating and waste-disposal lines project 1 ft from the floor and are laid in a communication trench leading to the opposite station.

The liquid wastes from each pair of stations run to a header leading to the waste-treatment area underground tanks. Five of the six smaller lines shown are for the five types of waste noted earlier; the sixth is a spare. It is intended that the type C waste line (hydrochloric acid and/or solvent) contain a plastic tube which, instead of leading to the tanks, runs to a portable shield having a capacity of 5 gal and a weight of 2 tons.

Ventilation for both the inside and the outside of the equipment is provided. The 4-in. duct projecting from the floor can draw a maximum of 100 cfm of air and the 12- by 12-in. duct can draw a maximum of 1200 cfm of air. The former is connected directly to a vent on the particular experimental equipment, whereas the latter is connected to a canopy over or around the equipment. Air from the smaller duct is scrubbed and filtered in the waste-treatment area and is discharged into a stainless steel pipe running to the top of the reactor stack. Air from the larger duct passes through a pair of filters in the semiworks filter pit and is discharged in the system leading to the base of the stack.

The area adjacent to the projecting pipes and ducts is shielded by two layers of 3-in. steel slabs, which are removable as are the 18-in.-thick concrete trench covers.

The area bounded by the shallow steel frame is sprayed with G. E. Cocoon to seal up the crevices. A plastic floor tile with removable underlayment protects the concrete floor from spills, and three floor drains are provided for nonactive waste, which is continuously monitored.

DECLASSIFIED

Safety showers are located at each end of the semiworks area, and the end constituting the west end of the building has an emergency exit door.

Lighting for the area is supplied by ceiling-supported incandescent lamp fixtures, which have reflectors which are easy to clean. Several CO_2 fire extinguishers are located throughout the area.

At the present time three experiments are set up at five of the eight work stations. None has, as yet, progressed to the stage of requiring shielding.

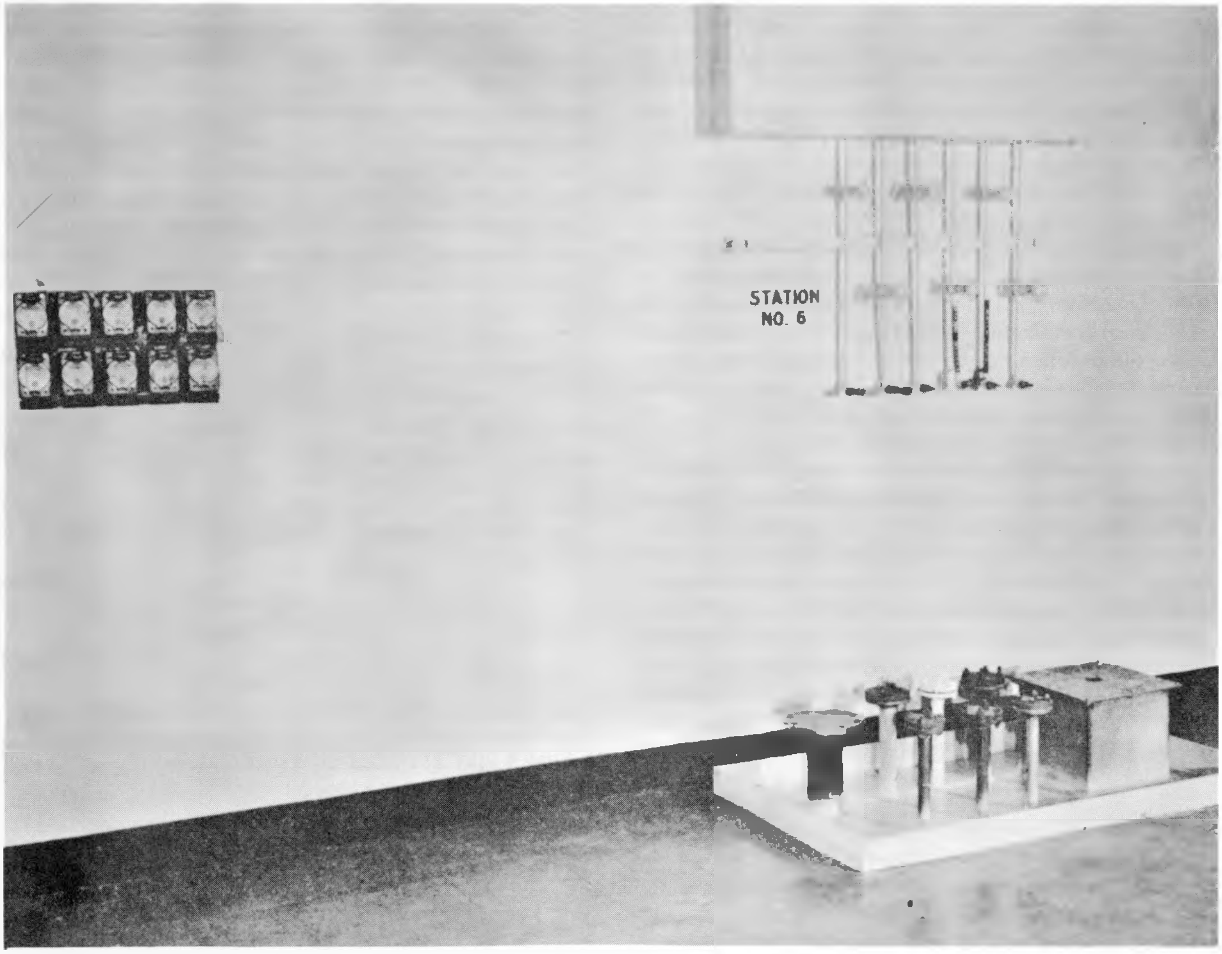


Fig. 6—View of one of the stations in the semiworks area showing services and drain lines.

Semihot Laboratories

In order to supply facilities for working with intermediate levels of radioactivity up to approximately 1 curie of 2-mev γ radiation, the semihot laboratories were developed.

These cells fill the position between the complex, heavily shielded hot cells and the small dry boxes.

Each semihot laboratory, of which there are five in the Brookhaven Hot Laboratory, consists of an 11- by 13-ft room, in which there is a shielded bench, simple laboratory bench and sink, and necessary laboratory utilities, including electric power, compressed air, vacuum, and hot, cold, and distilled water.

The semihot bench is essentially a 6-in.-thick steel bench top, divided in the center by a loading well opening beneath the bench. Extending across the bench front is a steel curb 3 in. high on which shielding brick may be piled at will to form a barrier as high as 6½ ft above floor level. Necessary manipulations are effected by reaching over the shielding wall through an 11-in. adjustable opening.

To permit use of the bench as a dry box, to prevent contamination of the shielding wall, and to assist in ventilation control, a sliding sash is located between

124/10

DECLASSIFIED

the bench proper and shielding-wall ledge. This sash can be fitted with glove ports. Illumination is provided by fluorescent fixtures above the bench which are isolated from the working volume by a sloping glass ceiling.

The ventilation[1] is so arranged that air is always flowing into the semihot bench from the room. This is accomplished by means of an exhaust blower (one for each semihot laboratory), located in a separate room behind the cells, which maintains a constant suction on the bench volume and exhausts this air through CWS 6 filters into a monitored air duct to the pile stack.

The air intake to the blower is baffled to eliminate dead air pockets in the bench, and adjustable louvers in the sash and near the bench top provide additional means of adjusting air flow to suit experimental requirements.

To make possible the introduction and removal of experimental equipment and materials while a shielding wall is in place, a remotely operated mechanism is built into each cell which will elevate stainless steel trays from the bottom of the well to bench level, traversing the bench horizontally to place equipment where it is needed. Up to four equipment trays can be accommodated in one semihot bench.

Each bench half contains shielded and coded drain lines to receive the different classifications of waste solutions. These shielded drains make it unnecessary to hold up quantities of liquid waste or to run long shielded waste lines.

Figure 7 is a photograph of a test run of the semihot bench mechanism. The operator is using the portable electrical control panel to elevate a tray of equipment from the well up to bench level where it will travel to working position. In an actual experiment additional shielding would be placed between the equipment and the operator and viewing would be accomplished by means of mirrors.

Figure 8 is a front and side section drawing of the semihot bench.

The cells were designed to have maximum experimental versatility, and the numerous uses to which they are, and can be, put are still being expanded.

Pneumatic-tube Room

The pneumatic-tube room is designed to receive carriers, popularly known as "rabbits," containing irradiated material from the pile. Remote-control handling equipment is provided for removing the material from the rabbit and depositing it in a shielded container in which it may be transported to any desired section of the hot laboratory for processing.

On the arrival of the irradiated material at the hot laboratory end of the tube system, the pneumatic valve is opened and the rabbit falls gently into a special metal basket directly under the tubes. This basket, mounted on tracks, is then moved to a position directly under a remotely controlled device which removes the screw cap of the rabbit. This device consists of a hollow stopper, which fits over the end of the cap, and a metal wedge inside this stopper, which fits into the screw slot in the cap. It is positioned electrically, and it mechanically unscrews and lifts the cap. Remotely controlled handling tongs then lift the inner container of irradiated material from the rabbit and drop it through a hole in the 3-in. floor shielding plate into the shielded container or pig. Throughout this operation, which requires about 1½ min, the operator remains approximately 2½ ft from the source and is further protected by 3 in. of steel. Mirrors are provided to give adequate visual coverage of this removal operation.

Air pressures are adjustable to give transit times between the pile and the hot laboratory of from several seconds to approximately half a minute.

Clean-up Areas

1. Decontamination Cell. The decontamination cell is the clean-up area designed to decontaminate large bulky apparatus by immersion in an appropriate solution. This room has two highly polished stainless steel floor tanks approximately 3 ft in diameter by 4 ft deep, protected by walls consisting of 12 in. of concrete with 3-in. steel doors. It is serviced by a monorail. A "marine" window, consisting of a transparent solution of zinc bromide (sp. gr. 2.5), is installed in the concrete wall of the decontamination cell. Through this window the operator may watch the decontamination operation in complete safety.

In order to charge the floor tanks with proper decontaminants, auxiliary equipment is required. This equipment consists primarily of a make-up tank, into which the fresh decontaminant is charged, and a transfer tank, which serves as an intermediate tank in the transfer of solutions to and from the make-up tank, the floor tanks, and the waste lines. Transfer is accomplished by means of air, vacuum, or auxiliary pump. A suitable valve manifold, liquid-level indicator, specific gravity manometer, and vacuum-pressure gauge with proper automatic safety valves are also provided. All potentially radioactive solutions are shielded.

2. Equipment-clean-up Room. Associated with each of the three hot cells and the semihot cells is an equipment-clean-up room. These rooms are intended for preliminary disassembly and decontamination of apparatus directly as it comes from either of these hot areas. To provide both the necessary facilities and the space for this operation, a stainless steel sink with both hot and cold water and a floor drain are installed in these otherwise bare rooms. The floor

DECLASSIFIED

slopes upward at the doors to prevent any straight through radiation.

If it ever becomes necessary to hose down the apparatus or the floor with a considerable amount of water, the raised edge will prevent flow of the resulting solution out of the room. As in the decontamination cell, the doors consist of 3 in. of steel and the walls of 12 in. of concrete.

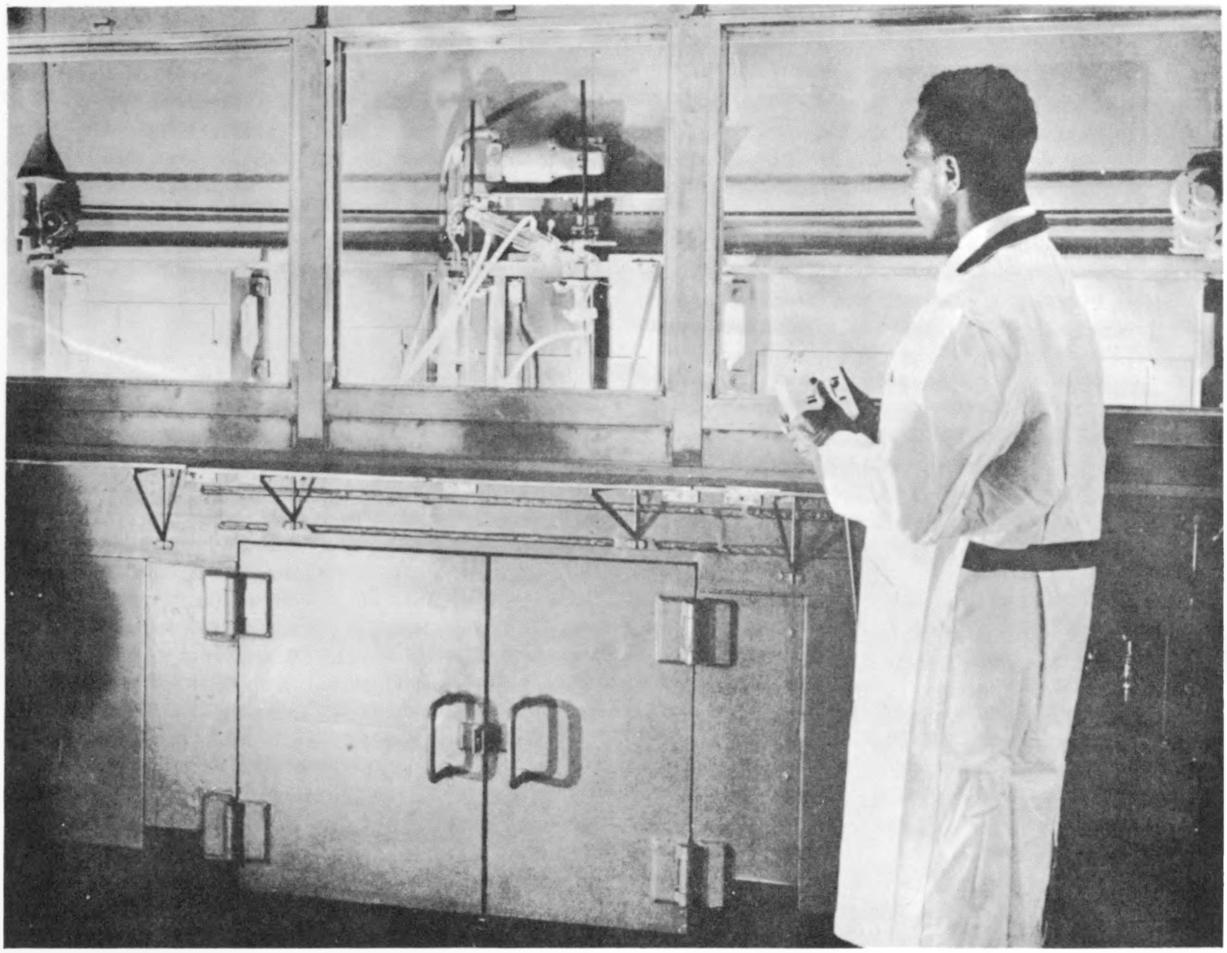


Fig. 7—Close-up view of shielded bench in one of the semihot laboratories with shielding wall removed to show direct view of equipment being moved into place by remote control.

Closed Dissolver System

Very nearly all uranium dissolver systems now in operation are open systems in that the noncondensable dissolver off-gases are immediately discharged to the atmosphere through stacks of varying heights. Because of the radioactive gas hazard involved, it is imperative that these gases be diluted sufficiently before they contact any form of animal life. In the populated locality around Brookhaven this restriction would demand the use of an exceptionally high stack to dilute the gases below tolerance concentrations, and even then under certain weather conditions dissolving would be prohibitive.

At Brookhaven it has been decided to attack the off-gas problem from a fundamental standpoint and to provide a storage and treatment system for the dissolver off-gases. Accordingly, a contract was made with Arthur D. Little, Inc., in early 1949 to determine the feasibility of such a system and to proceed with design details later. Their report was favorable and was the basis for the system as installed.

Essentially the system collects, absorbs, and stores the gases for a period of time sufficient to result in

126 1/2

DECLASSIFIED

atmospheric concentrations well below tolerance under all discharge conditions. The discharge of gas from this system can be controlled independently of the dissolving operation. The admission of air to the system is restricted to a practical minimum in order to increase the ratio of adsorbable to nonadsorbable gas stored. An increase in this ratio results in a longer decay period and a correspondingly lower discharge concentration. By employing this system of storage, it should be possible to reduce the accumulation of long-lived daughter activity, having gaseous parents, in the vicinity of the laboratory.

The primary function of this system is to furnish a uranium solution which can be further processed in other equipment for the separation of a specific fraction of fission products. The maximum working capacity of the dissolver tank is 12 gal of solution containing approximately 25 lb of uranium, or 1 to 10 special slugs. All the critical components in the system are fabricated of stainless steel; no glass equipment is used.

The details of design, together with test data, will be given in a separate paper in the near future.

Liquid-waste Handling and Storage System

The radioactive-liquid-waste system for the BNL reactor complex is designed to handle the liquid wastes from the reactor, reactor laboratories, and hot laboratory. Contaminated wastes from other groups at the Laboratory are processed and stored with the reactor waste after delivery to the area in waste pots.

The waste has been divided into five general types as mentioned above, each of which is handled by a separate system. To recapitulate, the designations and definitions of these wastes are

A. Accountable metal waste containing uranium and fissionable material

B. Highly active chemical waste containing no accountable material

C. Contaminated waste which, because of volatile solvent or HCl content, cannot go through the waste system

D. Large-volume chemical wastes of low activity level which do not require shielding

F. Normally uncontaminated waste which is monitored for activity before disposal

1. Waste Collection and Treatment. All wastes from drains at the reactor faces, floor drains, and laboratory sinks run by gravity to F waste holdup tanks located at the hot laboratory building. All normally uncontaminated waste from the hot laboratory drains into 8000-gal holdup tanks, where it is sampled and monitored before being discharged to the sewer. Should a tank of F waste be contaminated, it is pumped to a D waste storage tank where it is held for future concentration.

The hot area of the hot laboratory is the only area which is completely connected to the waste holdup area by piping. All the piping is of stainless steel all-welded construction and is laid in concrete trenches with removable concrete cover slabs. Any pipe leakage drains to the waste area where it is collected and identified.

Wastes are collected from three main locations in the hot laboratory, the hot cells, the semiworks area,

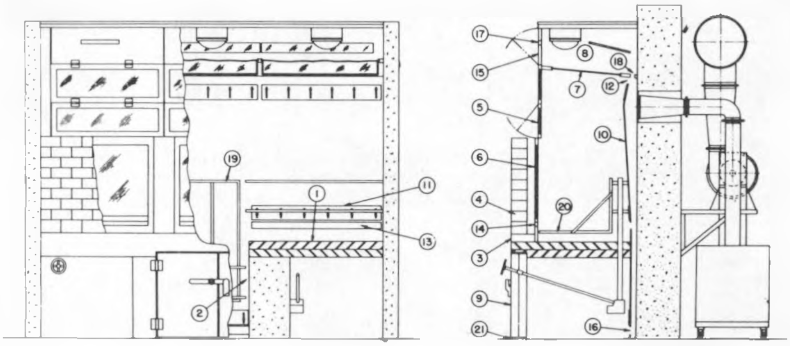


Fig. 8—Schematic drawing of shielded bench in a semihot laboratory.

1. Bench top
2. Loading well
3. Curb
4. Lead- or steel-brick barrier
5. Adjustable opening (main air inlet)
6. Sash
7. Glass ceiling
8. Fixture space
9. Steel door
10. Baffle
11. Adjustable vent cover
12. Upper baffle vent
13. Lower baffle vent
14. Sash vent
15. Fixture space access panel
16. Well baffle vent
17. Fixture space air inlet
18. Fixture space exhaust
19. Tray hoist
20. Tray
21. Well air inlet

127
13

DECLASSIFIED

and the semihot cells. The pipe trenches from these three areas have a junction point at the neutralization cell at the waste holdup area (Fig. 9). The pipes for A and B waste lead into the neutralization cell where the collection tanks for these wastes are located. The A type waste is collected in one of two 250-gal tanks, where it is held until a batch is ready for transfer to a neutralization tank. The B waste is collected in one 500-gal tank until a sufficient quantity is on hand for neutralization. The cell also contains an additional 250-gal tank that can be used as a spare system for either A or B type wastes. Neutralization of the waste

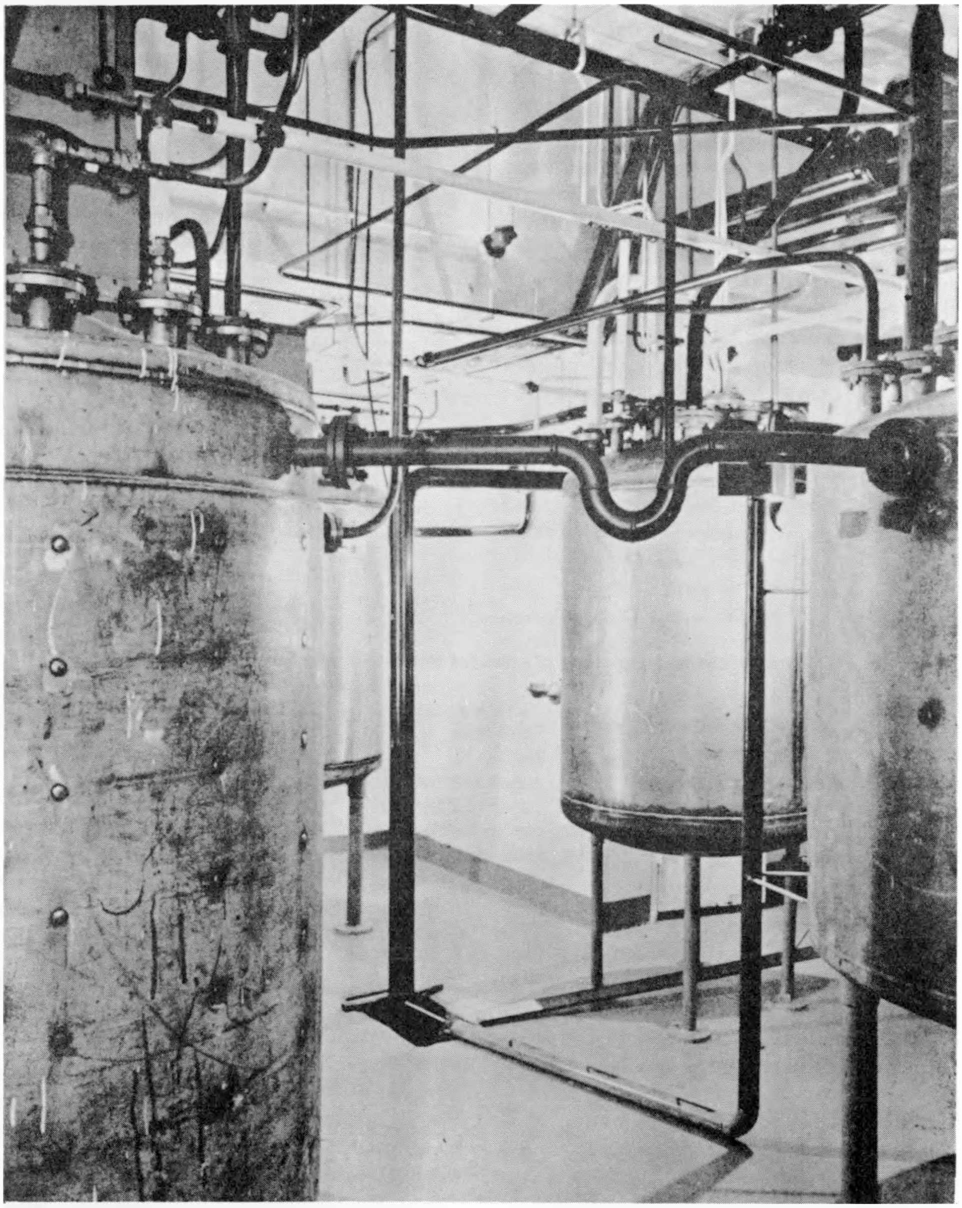


Fig. 9 — Liquid-waste-treatment area. Tanks, transfer lines, and instrument piping in neutralization cell for collection and treatment of highly radioactive wastes.

128
14

is carried out in a special 800-gal tank equipped with a jacket for either heating or cooling and with a mechanical agitator for complete mixing. After neutralization the wastes are transferred to the proper storage tanks.

All equipment in the neutralization cell is operated remotely from an instrument panel located above the cell. Waste transfers between tanks and from the cell to the storage tank farm are made with steam jets. Equipment is of stainless construction and is equipped with special facilities for decontamination purposes. All tanks and waste lines are vented through an off-gas system described below.

The D waste is collected in one of two 2000-gal tanks, where it is sampled and neutralized before being pumped to large storage tanks. If the pile canal should become contaminated owing to a ruptured slug, or from some other cause, the entire canal can be pumped directly to a D storage tank which is reserved for this purpose.

The F waste from the hot laboratory, before flowing into the collection tanks, passes through a drum trap, where large particles of solid matter are removed, and then through an automatic diversion system. The waste flows through a 50-gal tank, where it is mixed by means of a baffle. A Geiger-Mueller dipping tube is immersed in the center of the tank and connected to a low-level count rate meter. When the activity level of the F waste goes above a predetermined level, it actuates a motorized valve on the bottom of the tank, dumping the tank to the D system. The tank continues to fill and dump until the activity level of the F waste stream has returned to normal.

The wastes from all areas of the laboratory which are not connected to the collection system by piping are collected in special 5-gal waste pails and are trucked to the waste area where they are unloaded into the proper collection tank.

2. Waste-storage Tank Farm. The tank farm is located 600 ft north of the waste holdup area. All A, B, and D type waste is stored here. The tank farm is joined to the holdup area by means of pipes carried in a covered concrete trench, which prevents leakage from getting into the ground and also aids in the detection and location of leaks.

D waste is stored in two 100,000-gal above-ground tanks. A third tank is reserved for contaminated canal water. The tanks are all of mild steel construction and are coated on the inside with Amercoat chemical-resistant paint to protect them from corrosion. The tanks are located in an asphalt reservoir to prevent any leakage from getting into the ground undetected. It is ultimately planned to process the D waste through equipment for the removal of the solids and then by means of evaporation to remove the bulk of the water. The concentrate will be stored in underground tanks. Equipment for such a process is at the present time in the design and development stage.

The A and B waste is stored in six 8000-gallon stainless steel underground storage tanks. The tanks are connected by valved overflow lines which can be shut off for segregating the two types of waste. Each tank is enclosed in a concrete cubicle containing a sump, which is periodically monitored for tank leakage.

Hot Laboratory Fan House and Monitoring System

The hot laboratory fan house, located just north of the pile stack, has several functions in connection with the hot laboratory:

1. Exhausting ventilation air, "nonacid," from the hot area and discharging it into the base of the pile stack
2. Exhausting potentially acidic off-gases from hot laboratory equipment to the top of the pile stack
3. Monitoring ventilation air for radiation level of particulates, iodine, and xenon
4. Monitoring acid off-gases for radiation level of particulates, iodine, and xenon

The nonacid air originates in the hot laboratory from hood ventilation in semihot cells, station ventilation in the semiworks, and room and cell ventilation in the waste-treatment area. This air passes through CWS 6 filters at each of these sources to remove particulates and is then carried through a 42-in. concrete pipe to the fan house where it passes through two Wingfoil fans connected in parallel and is discharged into the base of the pile stack. These fans are set to maintain automatically −½ in. water pressure in the ducts of the hot laboratory by means of motor-controlled vanes on the suction side of the Wingfoil fans. Either one or both fans will operate automatically depending upon the load. Maximum capacity of both fans is approximately 30,000 cfm.

The acid off-gases are removed from the waste tanks, equipment in the semiworks, and hot cells. The gases are scrubbed with caustic in the waste-treatment area and are carried to the fan house in a 14-in. stainless steel duct. A 2500-cfm blower pushes the gases to the top of the pile stack. Another blower is connected in parallel as a standby and cuts in automatically in case of mechanical failure of the first blower.

The fan house is also equipped with a gasoline motor-generator set which starts automatically in case of power failure. The generator can carry a maximum load of the two nonacid fans and one acid blower. The circuit breakers, automatic change-over relays, vane relays, and switches for the fans are located in the fan house.

Two identical monitoring systems are installed in the fan house to check the acid and nonacid off-gas

DECLASSIFIED

streams for activity level before release to the atmosphere. Constant volume samples are metered by four Roots blowers. Two blowers draw off 5-cfm samples of the acid and nonacid air, pass it through high-efficiency filter papers, and return it to the ducts (Fig. 10). The filter papers are continuously counted for β-γ particulate activity, as well as α activity, with rate meters and scalers. The activity level is recorded on a Brown recorder.

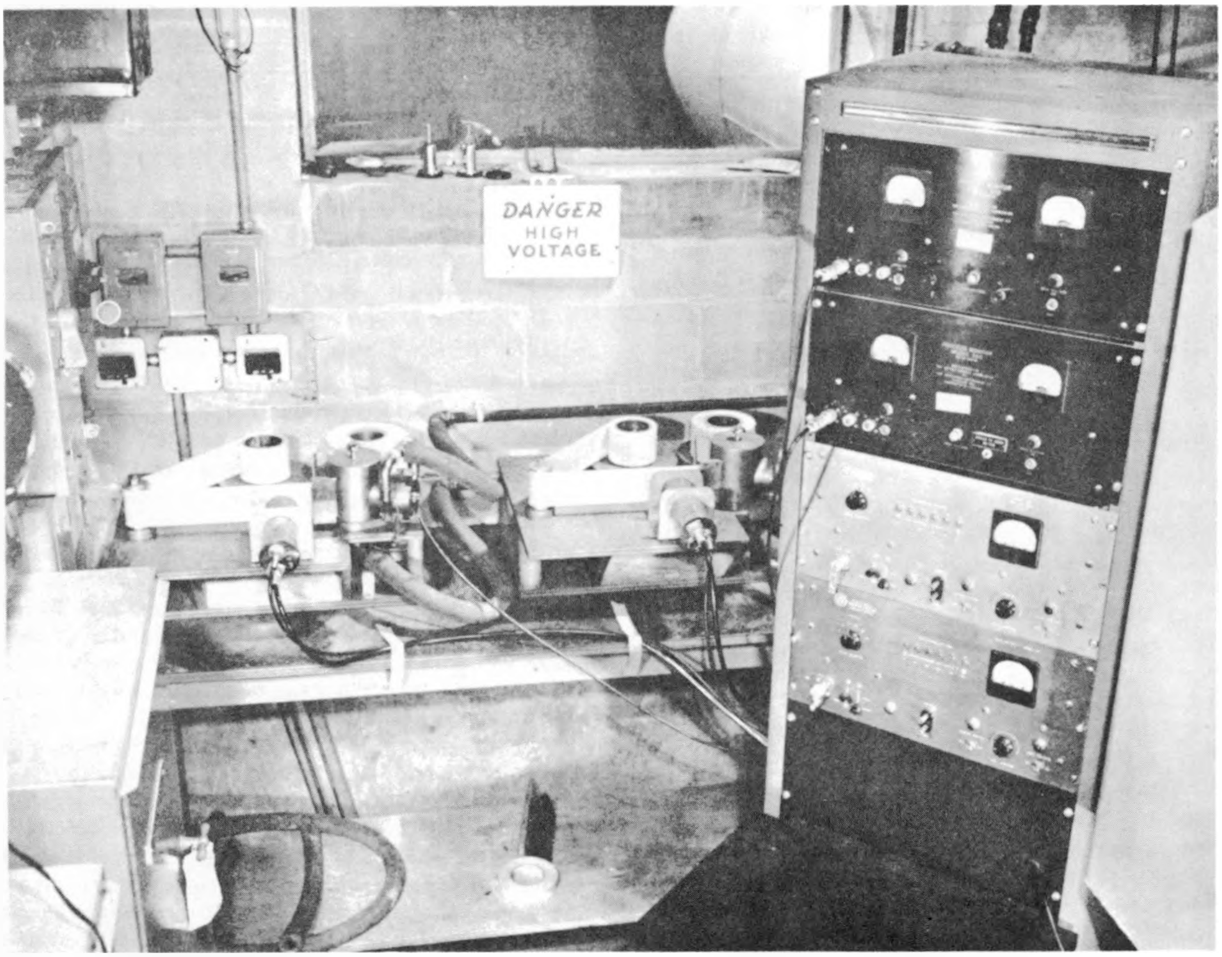


Fig. 10—Hot laboratory off-gas monitoring system. Moving tape filters and counting instrumentation for detection of radioactive particulate matter in off-gas streams.

The other two Roots blowers draw off two 3-cfm samples, one from the acid air and one from the nonacid air. Each sample is passed through a caustic scrubbing tower to remove the iodine. The caustic is continuously recycled through the tower to achieve a concentration factor of 4×10^4 on the iodine when it is at tolerance levels. The caustic flows past a Geiger-Mueller dipping tube connected to a rate meter. The build up of iodine activity in the caustic is recorded on the Brown recorder. The dipping tubes are located in 7-in. lead background shields, through which the caustic flows to a solenoid-operated piston recycle pump.

The acid and nonacid air leave their respective towers and pass through ionization chambers, and the air is returned to the main ducts. The ionization current due to xenon radiation is measured on a micromicroammeter and recorded on the Brown recorder.

Design levels of activity to be recorded by the monitoring system are

1. Iodine, 1×10^{-15} curies per cubic centimeter of air

130

16

2. Xenon, 1 × 10^{-13} curies per cubic centimeter of air
3. Particulates, 3 × 10^{-17} curies per cubic centimeter of air

The flow rates through both the acid and the nonacid systems are measured with Pitot-Venturi meters, and they are continuously recorded on a chart.

SUMMARY

The hot laboratory building described in the foregoing paper is now in operation at Brookhaven National Laboratory, and its various facilities have been found to perform satisfactorily for the purposes for which they were designed.

REFERENCE

1. John J. Keyes, Ventilation Studies on a Radiochemical "Semi-hot" Cell, Report BNL-27, Sept. 1, 1949.

April 1951

DECLASSIFIED

THE EXPONENTIAL EXPERIMENTS AT ARGONNE NATIONAL LABORATORY

By A. H. BARNES, B. HAMERMESH, and
B. I. SPINRAD
Argonne National Laboratory

C. KIMBALL
Michigan College of Mining and Technology

and N. L. KRISBERG
U. S. Air Force

Report TID-5025

ABSTRACT

The general theory of the exponential experiment is discussed, together with the detailed information available on a series of exponential experiments now taking place at Argonne. Data from a typical experiment are presented.

INTRODUCTION

An exponential reactor may be formally defined as a small reactor constructed so that leakage prevents a chain reaction even if the reproduction factor K is greater than 1. The name "exponential experiment" probably arose from the fact that the analytical solutions for the diffusion equation in a subcritical assembly always involve expressions of the form $e^{\pm z}$. Such an experiment gives considerable information on the behavior to be expected from a reactor. Not only does it serve to guide the construction of a particular reactor, but it also aids in improving reactor theory.

The fundamental reason for performing the early exponential experiments is contained in a quotation from a report[1] of the Columbia group:

> "This report concerns some experiments performed to ascertain whether a given lattice of uranium oxide lumps embedded in graphite could give a divergent chain reaction if its dimensions were made sufficiently large."

To be sure, we are no longer involved in determining whether a chain reaction can be obtained; however, the exponential experiment still remains one of the simplest methods of obtaining certain parameters needed for the design of reactors, and a large number of such experiments have been performed.[2]

The advantages of an exponential experiment are derived from the fact that it is a subcritical assembly. A source of neutrons must, therefore, be used to obtain a flux for activation measurements. Instrumentation and safety devices can be reduced since there is no danger of a divergent chain reaction. The material requirements are obviously less than those for a complete critical assembly.

In the first experiments the sources used were of the order of 0.6 to 2 g of radium mixed with beryllium. Stronger sources are more readily available now; a reactor may be used as a neutron source, or substitutes for radium with higher intensity can be obtained. In the experiments which are now being performed at Argonne, the CP-2 reactor, a copy of the original West Stands reactor, serves as the source.

DECLASSIFIED

Ordinarily an exponential assembly is kept at sufficiently low flux so that extensive shielding is not required. This, plus the fact that the assembly need not be cluttered with instruments and safety devices, provides flexibility in adapting the experiments to changes in reactor design.

While the exponential experiment has the advantages listed above, it also suffers from a number of disadvantages. Since it is fed by a source of neutrons, the flux level in the assembly is limited by the source strength and by the effective multiplication of the reactor. Activation experiments requiring a high flux must be performed in a critical experiment or in an operating reactor. The limited size of the exponential assembly frequently means that the results obtained must be extrapolated for application to an operating reactor. Finally, numerous effects which appear in the operation of a reactor cannot be easily simulated in an exponential experiment. These effects include such important ones as reactor kinetics, reactor control, temperature effects, and poisoning by fission products.

In general, it is probably correct to say that for reactor design an exponential experiment is most useful after the basic constituents of a reactor have been determined and when the most advantageous arrangement in the reactor core is to be found. The flexibility permits a relatively easy check of the effects of engineering changes on the physics of a reactor. Once the engineering of the reactor core has been frozen, either a critical assembly or a prototype reactor is more useful.

The present exponential experiments at Argonne are being performed to answer questions pertinent to the lattice design of a heavy water moderated, heavy water cooled, natural-uranium production reactor now known as CP-6. The experiments were undertaken after theoretical studies determined the desired constituents of the reactor core. The accuracy of theoretical calculations was not great enough to provide adequate performance data. Within several months the reactor design will be sufficiently frozen so that the exponential experiment can no longer provide further useful answers.

A summary of the data desired from the exponential experiment on CP-6 is perhaps typical of the range of problems which can be solved. First, the multiplication constant of a series of lattices was required to better precision than could be determined by theoretical estimates.

[redacted]

Second, the exponential experiments give precise information on the critical size of the system.

Third, the experiment assembly allows testing of the effect of reflectors, which is important in CP-6 in determining properties of external breeding blankets.

Fourth, simple control schemes may be tested in configurations where theory becomes too complicated.

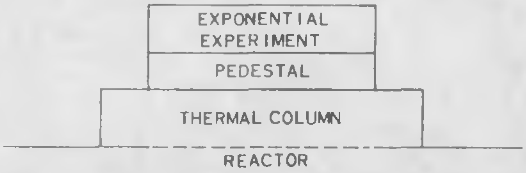
Fifth, preliminary estimates of temperature coefficient may be obtained.

Sixth, a good many reactor-theory parameters which enter into theoretical calculations (diffusion coefficients, disadvantage factors, and relaxation lengths) may be evaluated by detailed flux traverses.

THEORY

General Theory of the System

The sketch below shows a typical exponential experiment. Neutrons diffusing through the thermal column of a reactor enter the pedestal and serve as a source for the material under investigation in the exponential tank.



The theory of exponential experiments is obtained from solutions of the diffusion equation with appropriate boundary conditions. The differential equation for the neutron flux ϕ in a nonreproductive medium is

$$D\nabla^2\phi - \Sigma_a\phi = 0 \qquad (1)$$

where D = the diffusion constant

∇^2 = the Laplacian operator

Σ_a = the macroscopic absorption cross section

The boundary conditions limiting Eq. 1 are that ϕ and $D\, d\phi/dz$ be continuous.

The fundamental solution for a finite medium, such as the experimental tank, is given by

$$\phi = AJ_0\left(\frac{j_{01}r}{R}\right) \sinh \kappa(t - z) \qquad (2)$$

L^2, j_{01}/R, and κ are related by

$$\kappa^2 = \frac{j_{01}^2}{R^2} + \frac{1}{L^2} \qquad (3)$$

where $L^2 = D/\Sigma_a$

j_{01} = the first root of $J_0(x)$

t = height of the system

A more complete discussion of the solutions to Eq. 1 is given in Appendix A. A measure of the beam attenuation in passing through the tank is given in Eq. 2.

In multiplying mediums the thermal diffusion equation becomes

DECLASSIFIED

$$\nabla^2\phi + B^2\phi = 0 \qquad (4)$$

The solution of Eq. 4 is similar to that of Eq. 2, except that B^2 is substituted for $-1/L^2$, so that

$$B^2 = \frac{j_{01}}{R^2} - \kappa^2 \qquad (5)$$

In general, exponential experiments determine B^2 by measurements which give R^2 and κ^2. While B^2 is directly determined from the data, other constants of the medium must either be computed from B^2 or be observed from detailed measurements of the flux behavior. The interpretation of B^2 is discussed in the following section.

The neutron flux in the pedestal is not measured during each experiment since the pedestal is not an integral part of the lattice. However, the flux in the pedestal must be investigated in planning the experiment since the pedestal is used to damp irregularities in source flux. These irregularities arise from changes in the cross-sectional geometry of the system in going from the source to the experimental tank, or from asymmetries in the source. As a result the flux in the pedestal need be measured only once in a search for flux irregularities. Detailed calculations showing the effect of the pedestal are shown in Appendix A.

The measurements must be made at some distance from the boundaries because of the effect of matching a thermal source to a multiplying lattice. A treatment of this effect is given in Appendix B.

Theory of the Heavy Water Heterogeneous Exponential

The lattices under investigation here consist, basically, of natural-uranium rods suspended in heavy water. The properties of the lattices may be defined by the parameters

τ_f = the neutron age during that part of the energy range (near fission) in which slowing down is represented by a Yukawa kernel $e/r\ e^{-r/\sqrt{\tau}}$
τ_{e1} = the neutron age from the initiation of Gaussian slowing down to the top of the resonance absorption level in uranium
τ_{er} = the neutron age in the resonance absorption band
τ_{e2} = the neutron age from resonance to thermal
L^2 = the thermal diffusion area
K = the multiplication constant
p = the resonance escape probability
f = the thermal utilization factor
$\eta\epsilon$ = the number of fast neutrons formed by fission per thermal absorption in uranium
B^2 = the Laplacian of the lattice

It is apparent from Eq. 51 (Appendix B) that B^2 is identical with $\overline{k^2}$ of a two-group theory. In the energy breakdown listed above, with five groups of neutrons (one fast, three epithermal, and one thermal), B^2 is a more complicated expression. The Laplacian equation is

$$K = (1 + L^2B^2)(1 + \tau_f B^2) \exp\left[(\tau_{e1} + p\tau_{er} + \tau_{e2})B^2\right] \qquad (6)$$

In pure heavy water τ_f and $\tau_{e1} + \tau_{er} + \tau_{e2} \equiv \tau_e$ are known and have been evaluated[3] as $\tau_f = 48\ \text{cm}^2$ and $\tau_e = 79\ \text{cm}^2$. It may be shown that the corrections on τ_f and τ_e, due to resonance absorption and the presence of uranium, are small and virtually cancel for small volume fractions of uranium. The reasoning is as follows:

In general, for energy regions where cross sections are not varying too rapidly, $\tau \propto 1/(\Sigma_{tr})(\xi\Sigma_s)$, where Σ_{tr} is the macroscopic-transport cross section summed over all components of the system and $\xi\Sigma_s$ is the slowing-down cross section. In the fast range, ξ_U is very much less than ξ_{D_2O}, being roughly proportional to 1/A, where A is the atomic weight. On the other hand, Σ_{tr} for uranium is almost exactly double that for D_2O. The net effect of adding scattering and decreasing moderation is to keep τ_f virtually unchanged. In the epithermal range the scattering cross section of uranium does not quite balance the decrease in moderation, and hence the age tends to rise. However, for the range of τ_{er} we must replace τ_{er} by $p\tau_{er}$. Since $1 - p$ is roughly proportional to the volume fraction of uranium rods, it turns out that this absorption correction almost balances the scattering correction.

Therefore we may replace τ_f and $\tau_{e1} + p\tau_{er} + \tau_{e2}$ by the values for pure heavy water and obtain

$$K = (1 + L^2B^2)(1 + \tau_f B^2)\, e^{\tau_e B^2} \qquad (7)$$

The estimate of K given by Eq. 7 depends on values of L^2, τ_f, τ_e, and B^2, and the error of this estimate is dependent on errors in these parameters.

Another method of determining K may be obtained from the equation of neutron economy[4]

$$K = \eta\epsilon p f \qquad (8)$$

Let us assume that by addition of thermal poison to the system we have so reduced f that K = 1. This is determined by observation at $B^2 = 0$. The errors in Eq. 7 are given approximately by

$$\delta K = (L^2 + \tau_f + \tau_e)\delta B^2 + B^2\delta(L^2 + \tau_f + \tau_e) = M^2\delta B^2 \qquad (9)$$

since $B^2 = 0$. Here M^2, the migration area, has been defined as $L^2 + \tau_f + \tau_e$. Letting K_0 refer to the unpoisoned system and K_1 to the poisoned, we have

DECLASSIFIED

$$K_0 = \eta_0\epsilon_0 p_0 f_0$$

$$K_1 = \eta_1\epsilon_1 p_1 f_1 = 1 \qquad (10)$$

$$\eta_0 = \eta_1 \quad \epsilon_0 = \epsilon_1 \quad p_0 = p_1$$

The conditions on the last line state that the properties of the system for fast neutrons have remained unchanged. Then

$$K_0 = \frac{f_0}{f_1} K_1 = \frac{f_0}{f_1} \qquad (11)$$

is an estimate subject to error in B^2 (from $K_1 = 1 \pm M^2\delta B^2$) and in f_0 and f_1. In our case, where the only foreign elements in the system, heavy water and aluminum, have small, easily determined absorptions, f_0 may also be considered known. Equation 11 then gives a measure of K, subject to different errors from the estimate of Eq. 7.

It is also apparent that intermediate poisoning may be used. Combining Eqs. 7 and 10, we obtain for the general case

$$K_0 = (1 + L_1 B_1^2)(1 + \tau_f B_1^2)\, e^{\tau_e B_1^2} \frac{f_0}{f_1} \qquad (12)$$

Fitting the Experimental Laplacian Data

The estimate of the parameter B^2 is the fundamental measurement of the exponential experiment. So that Eq. 7 may hold, the B^2 used must be the Laplacian $(-\nabla^2\phi/\phi)$ measured over that part of a system which is far removed from boundaries.

The necessity for this condition of remoteness from boundaries lies in the fact that the solution of the equation for a subcritical assembly with source is a sum over the characteristic solutions of the exact reactor equations and exact boundary conditions, B^2 being the smallest eigenvalue. The higher characteristic functions are physically represented by perturbations of the flux shape and energy spectrum near boundaries. These higher-order functions decrease rapidly far from boundaries.

In the exponential experiment the flux in the center behaves as though it were a solution of Eq. 4. Likewise, since the mean free paths of neutrons vary with energy, the boundary conditions affecting Eq. 4 are energy dependent. The flux at the center conforms to some average boundary condition which, in theory, could be obtained by a suitable energy average of the monoenergetic boundary conditions. In practice, however, it is simpler to measure the coefficient of the Bessel function and the hyperbolic sine to which the flux may be fitted.

Although the system behaves as though it were a solution of Eq. 4, with solutions given by Eqs. 2 and 5, we do not know in advance the values of κ, R, and t. We must therefore make measurements of $\phi(r)$ at constant z and $\phi(z)$ at constant r, and we must fit the experimental points to Eq. 2. In so doing, we must take care not to measure too near the boundary, that is, within two or three mean free paths, or 5 to 10 cm for D_2O. With these measurements the problem is reduced to one of curve fitting.

1. Radial Fit. We are given a set of data f_i proportional to the flux for n radial positions r_i, and for constant z. The relative precision of the points is constant, and the relative errors ϵ_i have the same expectation values for each point. The data are to be fitted to a J_0 Bessel function of coefficient A and argument αr. The constant relative error ϵ is obtained by counting all foils to the same total counts. Hence, we may write the equation to be used

$$f_i(1 \pm \epsilon_i) = AJ_0(\alpha r_i) \qquad (13)$$

We may divide this equation by $J_0(\alpha_0 r_i)$, where α_0 is the best fit solution of Eq. 13, and obtain, to linear terms in differential quantities,

$$\frac{f_i}{J_0(\alpha_0 r_i)} - \frac{AJ_0(\alpha r_i)}{J(\alpha_0 r_i)} = \pm\,\epsilon_i A \qquad (14)$$

Equation 14 is a constant-expected-error equation, and hence we may, without further weighting, minimize the sum of the squares of ϵA by variation with respect to A and α. Then

$$\frac{\partial}{\partial A}\sum_i \left[\frac{f_i}{J_0(\alpha_0 r_i)} - \frac{AJ_0(\alpha_0 r_i)}{J_0(\alpha_0 r_i)}\right]^2 = \frac{\partial}{\partial\alpha}\left[\frac{f_i}{J_0(\alpha_0 r_i)} - \frac{AJ_0(\alpha r_i)}{J_0(\alpha_0 r_i)}\right]^2 \qquad (15)$$

Performing the indicated operations, eliminating A from the equations, and recalling that $\alpha = \alpha_0$ for best fit, we get

$$\frac{1}{n}\sum_i \frac{f_i}{J_0(\alpha_0 r_i)} \sum_i r_i \frac{J_1}{J_0}(\alpha_0 r_i) = \sum_i \frac{f_i}{J_0(\alpha_0 r_i)}\, r_i \frac{J_1}{J_0}(\alpha_0 r_i) \qquad (16)$$

as a transcendental equation to be solved for α_0.

We solve Eq. 16 in the following way: Let α be a first guess at the solution. Define

$$A_i \equiv \frac{f_i}{J_0(\alpha r_i)}$$

$$\bar{A} \equiv \frac{1}{n}\sum \frac{f_i}{J_0(\alpha r_i)} \qquad (17)$$

Assuming $\alpha_0 - \alpha$ to be an infinitesmal, we expand $\frac{J_0(\alpha r_i)}{J_0(\alpha_0 r_i)}$ to one term, after substituting Eq. 17 into Eq. 16. We then get, after some calculation,

$$\alpha_0 = \alpha + \frac{\sum_i A_i F - \bar{A} \sum_i F}{\left[\frac{1}{n} \sum_i A_i F\right] \left[\sum_i F\right] - \sum_i A_i F^2} \tag{18}$$

where $F = r_i \frac{J_1}{J_0} (\alpha_0 r_i)$

This is a first order solution. Replacement of α_0 by α in the summation terms of Eq. 18 does not change the order of validity of the approximation nor does replacement of A_i by $\bar{A}$ in the denominator.

We may then finally write

$$\alpha_0 = \alpha + \frac{\sum_i r_i \frac{J_1}{J_0}(\alpha r_i) \left(\frac{A_i}{\bar{A}} - 1\right)}{\frac{1}{n}\left[\sum_i r_i \frac{J_1}{J_0}(\alpha r_i)\right]^2 - \sum_i \left[r_i \frac{J_1}{J_0}(\alpha r_i)\right]^2} \tag{19}$$

To check Eq. 19 we observe that $\alpha_0 = \alpha$ if, and only if,

$$\frac{\sum_i r_i \frac{J_1}{J_0}(\alpha r_i) \frac{f_i}{J_0(\alpha r_i)}}{\frac{1}{n} \sum_i \frac{f_i}{J_0(\alpha r_i)}} - \sum_i r_i \frac{J_1}{J_0}(\alpha r_i) = 0$$

which is equivalent to Eq. 16. As a result, we may define an iterative process, whereby α_0 is reinserted into Eq. 19 as α and a new α_0 is computed, until convergence is attained to within some desired criterion of smallness for $\alpha_0 - \alpha$. Mathematically, this process is equivalent to solving Eq. 16 by Newton's method, using approximations for the derivative.

The advantages of this method of solution are (1) examination of the A_i for smoothness leads to the observation of any bad experimental points without the necessity of plotting; (2) since the $r_i\ (J_1/J_0)(\alpha r_i)$ have the force of a weighting function only, they may be computed, without loss of precision in the estimate of α_0, to comparatively few significant figures; (3) the precision to which α_0 is desired sets a limit on the number of places to which A_i/A must be computed; and (4) it involves a characteristic feature of Newton's method, that the rate of convergence increases at every step for a smooth function and that a good guess is rewarded by one-step convergence.

2. Axial Fit. The fitting of the axial equations involves a fit to a three-parameter system of the form

$$f_i(1 \pm \epsilon_i) = A \sinh \kappa (t - z_i) \tag{20}$$

This fitting is tedious if all parameters are to be obtained simultaneously. However, the systems measured are all of such a sort that for the bulk of the points $\kappa(t - z_i)$ is large. Under these conditions, an approximation to Eq. 20 is

$$f_i(1 \pm \epsilon_i) = \frac{A\, e^{\kappa t}\, e^{-\kappa z_i}}{2} \tag{21}$$

While Eq. 21 is not useful in fitting, it demonstrates that the best value of κ is relatively independent of the choice of t; variation of Eq. 21 produces a value of κ which is completely independent of t.

Moreover, measurements of height of the system combined with theoretical studies of extrapolation distance give us a good estimate of t. Hence, we may use this value and treat Eq. 20 as a two-parameter system in A and κ. Having obtained κ in this way, we may, if desired, treat Eq. 20 as a two-parameter system in A and t. A reiteration is rarely required.

As in the radial case, we define κ_0 as the best fit value of κ, divide Eq. 20 by $\sinh \kappa_0(t - z_i)$ to obtain a uniformly weighted system, and vary the sum of the squares of the residuals with respect to A and κ. Eliminating A as before and remembering that $\kappa = \kappa_0$ is the solution, we get

$$\frac{1}{n} \sum_i \frac{f_i}{\sinh \kappa_0(t - z_i)} \sum_i (t - z_i) \coth \kappa_0(t - z_i) = \sum_i \frac{f_i(t - z_i) \coth \kappa_0(t - z_i)}{\sinh \kappa_0(t - z_i)} \tag{22}$$

The method of solution is the same as for the radial fit. Define

$$A_i \equiv \frac{f_i}{\sinh \kappa (t - z_i)} \qquad \bar{A} \equiv \frac{1}{n} \sum_i A_i \tag{23}$$

where κ is a trial value. Then Eq. 22 becomes

$$\sum_i (t - z_i) \coth \kappa_0(t - z_i) \left[\frac{1}{n} \sum_i A_i \frac{\sinh \kappa (t - z_i)}{\sinh \kappa_0(t - z_i)} - A_i \frac{\sinh \kappa (t - z_i)}{\sinh \kappa_0(t - z_i)}\right] = 0 \tag{24}$$

DECLASSIFIED

We may immediately replace coth $\kappa_0(t - z_i)$ with coth $\kappa(t - z_i)$ and expand $\frac{1}{\sinh \kappa_0(t - z_i)}$ to linear terms in $\kappa_0 - \kappa$. We then solve for κ_0

$$\kappa_0 = \kappa + \frac{\sum_i R_1 \, (R_2 - 1)}{\sum_i R_1 \left(R_2 R_1 - \frac{1}{n} \sum_i R_2 R_1\right)} \qquad (25)$$

where $R_1 = (t - z_i) \coth \kappa(t - z_i)$ and $R_2 = A_i/\bar{A}$. Approximating $A_i/\bar{A} = 1$ in the denominator, we finally get

$$\kappa_0 = \kappa + \frac{\sum_i R_1 \, (R_2 - 1)}{\sum_i R_1^2 - \frac{1}{n} \left(\sum_i R_1\right)^2} \qquad (26)$$

Having obtained κ_0 by this method, t_0 may be obtained from

$$t_0 = t + \frac{\sum_i \kappa_0 \coth \kappa_0(t - z_i) \left(\frac{B_i}{\bar{B}} - 1\right)}{\sum_i \left[\kappa_0 \coth (t - z_i)\right]^2 - \frac{1}{n} \left[\sum_i \kappa_0 \coth \kappa_0(t - z_i)\right]^2} \qquad (27)$$

where t is a first approximation to t_0 and B_i and $\bar{B}$ are defined by

$$B_i \equiv \frac{f_i}{\sinh \kappa_0(t - z_i)} \qquad \bar{B} \equiv \frac{1}{n} \sum_i B_i \qquad (28)$$

EQUIPMENT

The most useful piece of equipment for an exponential experiment is a reactor. It may be used to test the uranium and to serve as a source of neutrons. Strong photoneutron sources might be used as a substitute for the reactor if necessary. However, the reactor is a very convenient source because the power level is easily adjusted to give a convenient irradiation time.

Any uranium used should be tested for uniformity by the danger-coefficient method or some equivalent test. Chemical procedures are too lengthy and laborious, and they do not account for possible voids in the metal. Also, since only small pieces of the metal would be examined in the chemical procedures, these methods do not ensure the sampling necessary for large quantities of metal.

In general, the reactor or source neutrons are fed into the experiment through a thermal column. In order to predict the flux level of the exponential lattice it is necessary to know the flux level in the reactor as well as the attenuation in the thermal column and the pedestal. The thermal column in CP-2 is a square graphite column 5 ft long. This gives an axial attenuation constant of

$$\kappa = \sqrt{2\left(\frac{\pi}{152.5}\right)^2 + \left(\frac{1}{50}\right)^2} = 0.035$$

where $2(\pi/152.5)^2$ is the first eigenvalue of the boundary value problem for the x and y directions and $(1/50)^2 = 1/L^2$ for graphite. Thus the attenuation in a 5-ft length of this column is approximately

$$A_c = e^{-0.035 \times 152.5} = e^{-4.96} = 0.007$$

This square column feeds a circular graphite pedestal 5 ft in diameter and 2 ft long. This circular section is designed to match the 5-ft aluminum tank used to contain the exponential proper and the square column which is an integral part of the reactor as originally constructed. It is sufficiently long to attenuate higher harmonics produced by the square-circle mismatch to below 1 per cent of the fundamental. The circular column again attenuates the beam according to the attenuation constant

$$\kappa = \sqrt{\left(\frac{2.4048}{78.2}\right)^2 + \left(\frac{1}{50}\right)^2} = 0.0366$$

where 2.4048 = the first root of J_0
78.2 = the effective radius of the column (including the extrapolated length)
$(1/50)^2 = 1/L^2$ in graphite

The attenuation in the pedestal is

$$A_p = e^{-0.0366 \times 61} = e^{-2.23} = 0.11$$

The flux that could be supplied by CP-2 was approximately 1.6×10^8 neutrons/sec/cm^2/kw at the base of the thermal column. When a nonreproducing lattice was in the exponential tank, the attenuation produced by the thermal column and pedestal reduced the flux to about 1.2×10^5 neutrons/sec/cm^2/kw. When a reproducing lattice was in the tank, the flux levels were higher. For example, when single 1-in. rods were used with a 4.9-in. square, the multiplication was approximately 9 times.

The irradiation time was usually of the order of 10 to 20 min. The reactor power was chosen so that the foils would yield 10,000 counts in 2 to 3 min in the counting geometry used. The reactor usually operated at 2 to 10 kw, depending on the K of the multiplying lattice. For a corresponding nonmultiplying lattice the power was raised by a factor of 10. For cadmium ratio studies the power level was also raised by this same factor. For poison or control-rod studies the power had to be raised by a factor that depended on the amount of absorber that was added.

A mismatch again occurs at the base of the aluminum tank, introducing higher harmonics which serve to limit the depth in the tank at which accurate measurements can be made independent of harmonic corrections. A solution of this problem presented in Appendix A shows that these harmonics are generally well below 1 per cent of the fundamental at a height two diffusion lengths above the base of the tank. The diffusion length in this case is that of the exponential material.

The experimental tank (Fig. 1) was fabricated by forming and welding 61S aluminum sheet, 0.25 in. thick, into a cylinder 5 ft in diameter and 6 ft high. The bottom of the tank was a standard dished end, 0.25 in. thick, welded to the side wall. The walls were reinforced by four $\frac{1}{2}$ by 2 in. aluminum rings welded to the outer surface and spaced at 1-ft intervals. Measurements of the inside diameter, made after the tank was in its final position, indicated that its inside diameter was uniform to ±0.062 in.

The tank was closed at the top with a flat 1-in.-thick aluminum cover plate which bolted to the upper tank flange. A tight seal was provided by a $\frac{3}{8}$- by $\frac{3}{8}$-in. groove type neoprene gasket. The hold-down bolt holes on the cover plate were arranged so that the plate could be set in positions 90 deg apart.

To provide access to the interior of the tank for insertion and removal of measuring foils, a channel $3\frac{1}{2}$ in. wide by $57\frac{1}{2}$ in. long was cut in the cover plate along a diameter. This channel was closed with an aluminum housing which was bolted to the cover plate and was sealed with a flat neoprene gasket. Eleven rectangular slots were cut in the channel housing. These secondary openings were closed over with flat aluminum plates held down on gaskets with wing screws.

The main cover plate also contained a 10-in.-diameter glass window for observation of the interior of the tank.

The level of the water in the tank was determined by means of a sight glass which extended 42 in. to a point 6 in. from the top flange. The D_2O entrance and exit was through a 2-in. flanged aluminum fitting welded to the tank bottom near the perimeter.

The tank was located on top of the thermal column of the CP-2 reactor. To minimize contamination of the D_2O by H_2O vapor in the air when the cover plate was removed, an air-conditioned room 20.5 ft square, enclosing the tank, was constructed on top of the reactor shield.

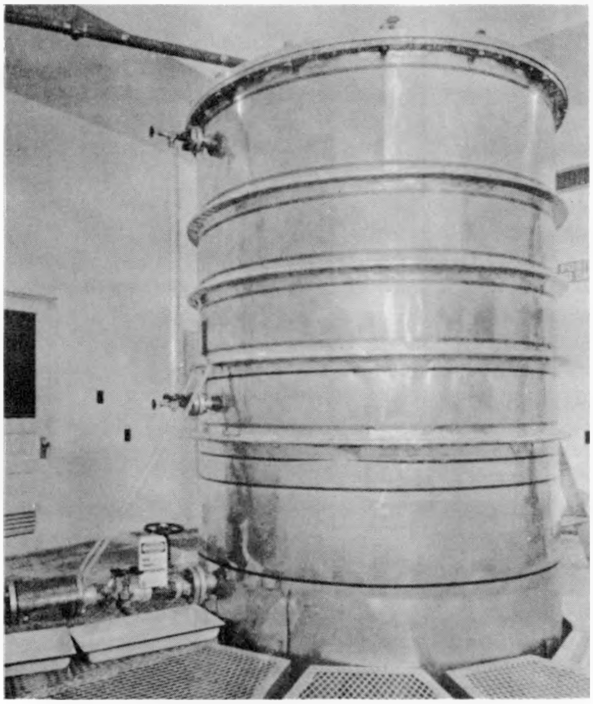


Fig. 1—Exterior view of the experimental tank. The tank is covered with 0.030-in. sheet of cadmium to prevent reflection of thermal neutrons. On the left side of the tank the D_2O release valve, the water-level indicator, and the He flush line can be seen. The metal grating at the bottom of the tank covers the lead pan which serves as an emergency container.

In order to permit rapid removal of the D_2O from the experimental tank, a storage tank was set up on the main floor of the CP-2 reactor room. This tank was a standard steel 900-gal tank with dished bottom and cover plate. It was pressure tested to 100 psi. The tank was 5 ft in diameter and 6 ft high and was fabricated from 0.50-in.-thick carbon steel. The entire inner surface was given a Heresite coating.

The general layout of the experiment is shown in Fig. 2. The storage tank was connected to the experimental tank with a 2-in. stainless steel pipeline. This line included a system of valves adjacent to each tank, which permitted the isolation of the line, as well as a

DECLASSIFIED

bellows expansion joint near the outlet from the experimental tank to remove stresses on the aluminum fittings. Transition from stainless steel to aluminum pipe was through aluminum-gasketed flanges.

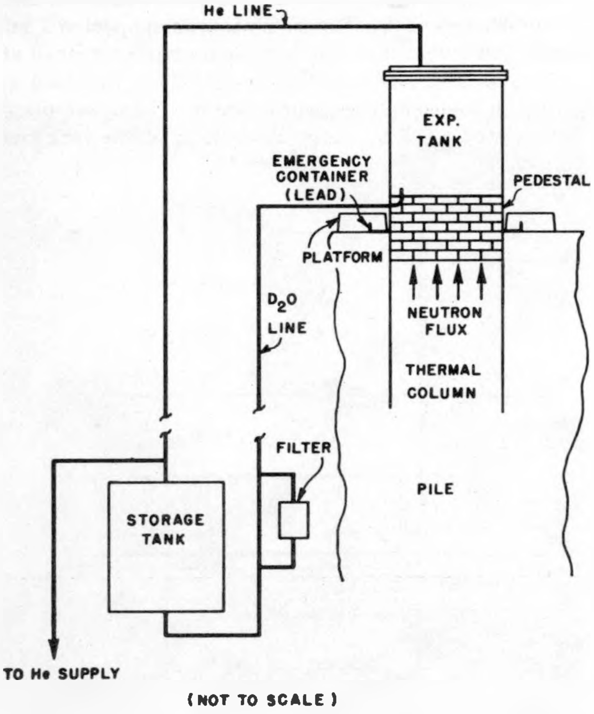


Fig. 2—Schematic diagram of the exponential experiment. A helium pressure system instead of a pump is used for transferring the water from the lower to the upper tank in order to avoid contaminating the D_2O.

This line also contained a porcelain thimble type filtering unit located adjacent to the lower tank but set slightly above the maximum level of water in the tank. A set of by-pass valves permitted water to ascend the pipe without passing through the filter element. When water from the upper tank was draining into the lower tank, it could be made to flow through the filter. Filter elements could be changed while the water was in either tank.

A helium atmosphere was maintained above the D_2O surface in each tank. The helium was fed into the top of the storage tank after it had passed through a freeze-out trap to remove any H_2O vapor present. The trap consisted of a 10-turn helix of ¼-in. stainless steel tubing immersed in a mixture of dry ice and trichlorobenzene. Three traps of this type were connected in parallel.

The storage tank and the experimental tank were also connected with a stainless steel pipe which ran from the top of the storage tank to the cover plate of the experimental tank. The purpose of this line was to maintain equal gas pressures in the two tanks when the D_2O was being drained from the upper to the lower tank. When closed, a valve in this line above the storage tank permitted helium pressure to be built up in the storage tank.

After the system had been repeatedly flushed with dry helium, the storage tank was filled with approximately 7000 lb of D_2O of 99.82 per cent purity. This was accomplished by blowing the D_2O from the shipping drums into the storage tank through a ⅜-in. stainless steel tube which fed into the top of the tank. Dry helium was used to displace the D_2O in the drums. The valve in the gas line above the storage tank was then closed, and the valves in the water line were opened. Dry helium was then fed into the storage tank at the top, forcing the water to rise and fill the experimental tank. The displaced helium in the upper tank was allowed to escape into the air through a valve on the tank cover plate. D_2O vapor in this exhaust helium was recovered by passing it through a freeze-out trap.

The level of the D_2O in the upper tank was determined by sighting with a cathetometer on the D_2O meniscus. When the desired water level was reached the valve on the water inlet was closed and the helium was then vented from the lower tank through a freeze-out trap. After atmospheric pressure had been reached in the lower tank, the valve in the gas line above the storage tank was opened so that, when the water was drained into the lower tank, a vacuum would not be produced in the upper tank.

In order to ensure that the upper tank pressure could not vary appreciably from atmospheric pressure, a safety valve in the form of a toy rubber balloon was attached to a tube extending from the tank cover plate. Any substantial increase or decrease in pressure within the tank caused the balloon to break and thus relieved the pressure difference.

The procedure for draining the experimental tank was to open the valve in the water line adjacent to the tank and allow the water to pass to the storage tank. The gas line allowed the helium pressures to equalize as the water flowed from one tank to the other.

The experimental tank was mounted upon an extension of the CP-2 thermal column which was carried upward to a point 2 ft above the top of the upper shield. The pedestal so formed was built up of graphite blocks arranged so that there were three stringers located as shown in Fig. 3.

The entire outer surface of the tank and pedestal was covered with a layer of 0.030-in.-thick cadmium sheet. The cadmium layer for the top of the tank was placed inside the tank. It was made up in the form of four quadrants, which were sealed in aluminum envelopes and laid on the tops of the uranium-rod handles.

As a safety precaution, a lead pan 15 ft in diameter and 1 ft deep was placed at floor level. The volume of this pan was sufficient to hold all the D_2O in case a leak should develop in the experimental tank. The lead pan extended through the graphite pedestal at floor level so that it would be impossible for any D_2O to leak down the thermal column.

A platform of expanded metal grating covered the lead pan. This platform was made of removable segments to permit access to the stringers in the pedestal.

The array of uranium rods rested on the tank bottom and was held in a vertical position by two aluminum plates through which the rods passed. Holes drilled through the plates located the rods in the lattice pattern being investigated. These plates were fabricated from 2S aluminum sheet ⅛ in. in thickness and 5 ft in diameter. The lower plate was supported 1 in. above the tank bottom on aluminum blocks spaced at eight points around the perimeter of the tank and at six other positions nearer the center. The upper plate was located 5 ft 2 in. above the bottom of the tank and was supported on an aluminum ring which had been welded to the inside of the tank wall. The lower plate was fixed in position with screws attached to the supporting blocks and the upper plate was clamped to its supporting ring. Figure 4 shows the rods assembled in the tank.

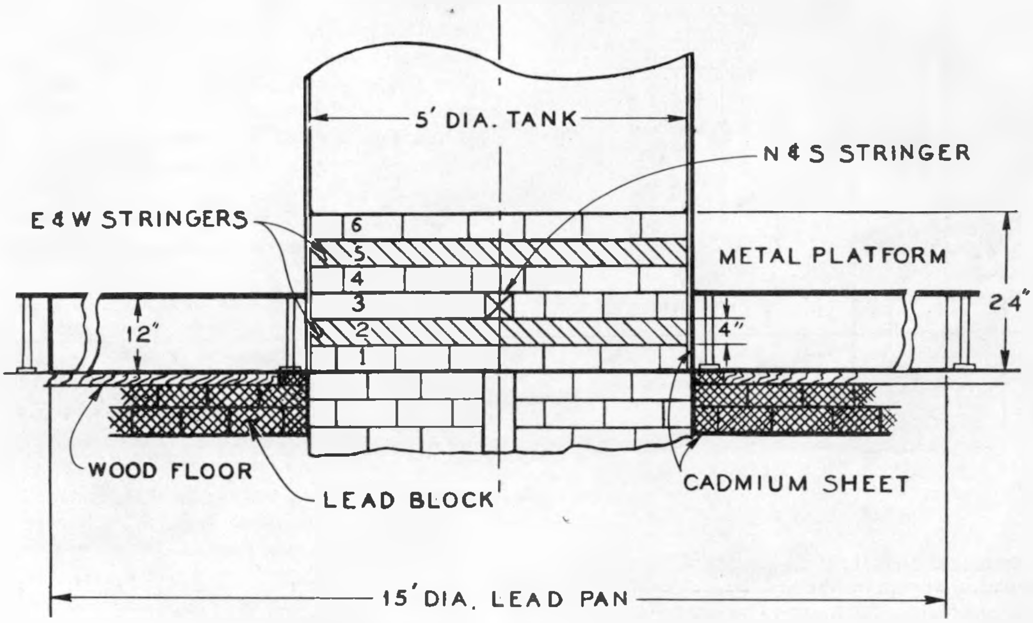


Fig. 3—Schematic drawing of the graphite pedestal. The removable stringers have foil slots for determining the flux in the pedestal. Asymmetry of the source neutron flux is most easily checked by pedestal measurements.

The metal loading in the tank was in the form of 1-in.-diameter uranium rods 5 ft in length. The rods were fabricated by the Argonne Metallurgy Division from metal obtained from Hanford for this experiment. Aluminum handles in the form of 1-in.-diameter ¹⁄₁₆-in.-wall tubing were attached to the uranium. During the early part of the work the uranium was left bare. Later it was jacketed with ¹⁄₃₂-in.-wall 2S aluminum.

Before the bare rods were exposed to D_2O all grease was carefully removed from them with trichlorobenzene, and they were passivated with dilute HNO_3 and then rinsed three times in distilled water. After being thoroughly dried they were loaded into the experimental tank. After jacketing, the rods were again cleaned with trichlorobenzene.

The foils used for flux measurements must be pure enough to give accurate results when saturated activities are computed after the long waiting periods following irradiation. This is true since in some irradiations there is a considerable spread in the intensity of activation of the different foils, for example, the monitor foil in an experiment involving cadmium-covered foils.

The foils should be sufficiently small so that the additional absorption introduced does not affect the

DECLASSIFIED

value of flux at the neighboring foil. The actual size will depend upon the macroscopic cross section of the exponential material. In the lattice of the 1-in.-diameter natural-uranium rods and D_2O moderator presently being studied at Argonne, indium foils 1 cm on a side and 6 mils thick, placed 10 cm apart, represent about 1 per cent of the cross section present due to the uranium.

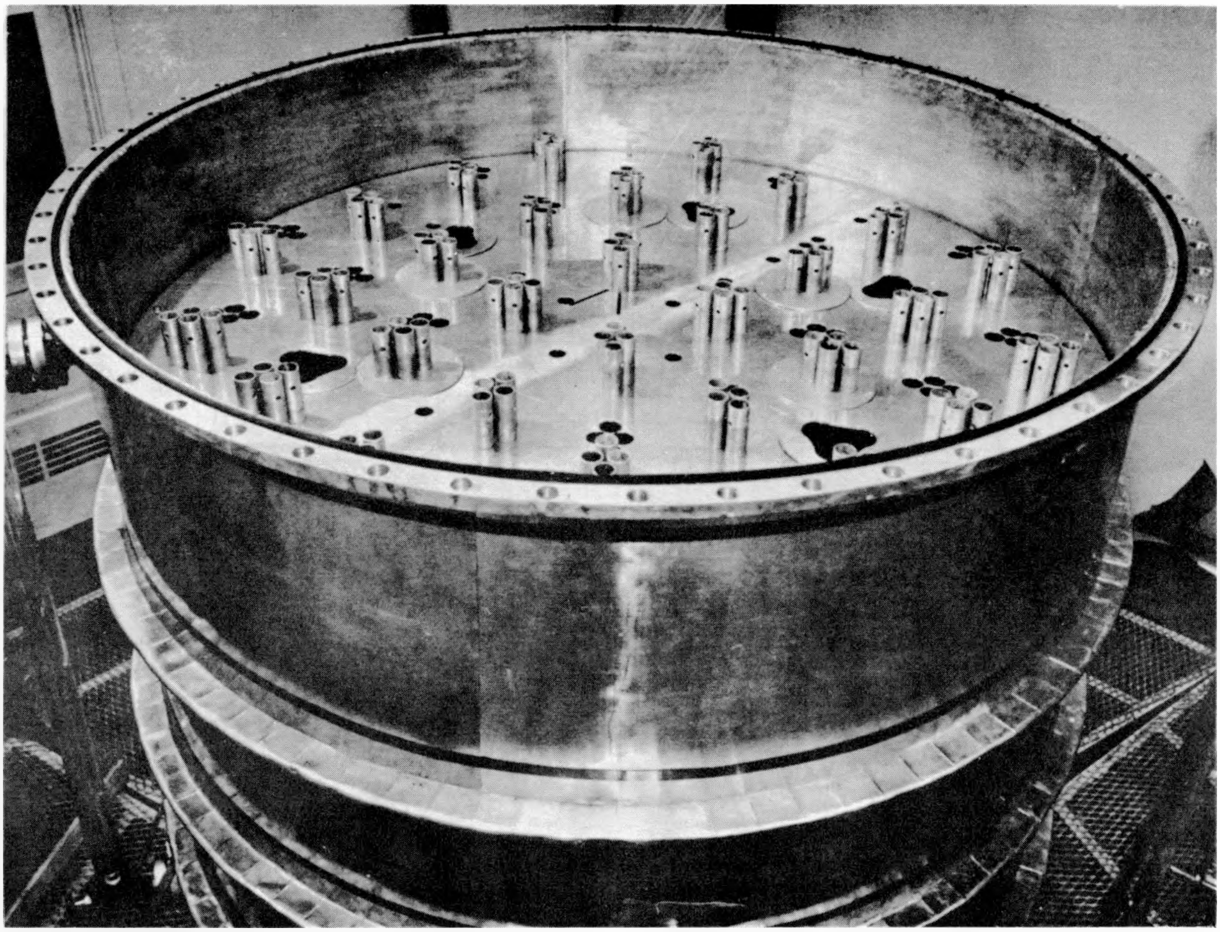


Fig. 4—Interior view of the experimental tank with a square lattice and a clump of four fuel rods at each vertex. The circular holes in the top plate position the vertical foil holders. The slits near one of the central clumps are used for flux-traverse measurements, and the rosette shaped holes are used for control-rod experiments.

In order to obtain results accurate to within about 1 per cent the relative positions of the foils must be known within about 0.5 mm. In some previous exponentials this accuracy has been obtained by taping the foils to a wire support and determining the relative positions with a cathetometer. However, this is usually a time-consuming procedure. In the present Argonne studies, a rigid aluminum ladder has been used with the foil positions accurately located by the machining and calibration of the support (Fig. 5). This ladder introduces less absorption per unit volume than does the indium foil. The ladder reduces the foil loading and positioning time from several hours to about 15 min. The position of the foil holders used for axial or radial runs in the assembly is determined by positioning holes in the aluminum plates located in the top and bottom of the tank. A key arrangement in the bottom plate provides proper radial orientation of the foils. An electrical contact on the foil holder determines all positions relative to the surface of the D_2O. As shown by the formulas, lengths $t - z_i$ are measured from the extrapolated height. The values of

$t - z_i$ are obtained by adding the extrapolation distance to the distances between the foils and the tip of the pointer set at the water surface. The positions of the foils used for flux traverses are determined from the points at which they are suspended from the upper aluminum plate.

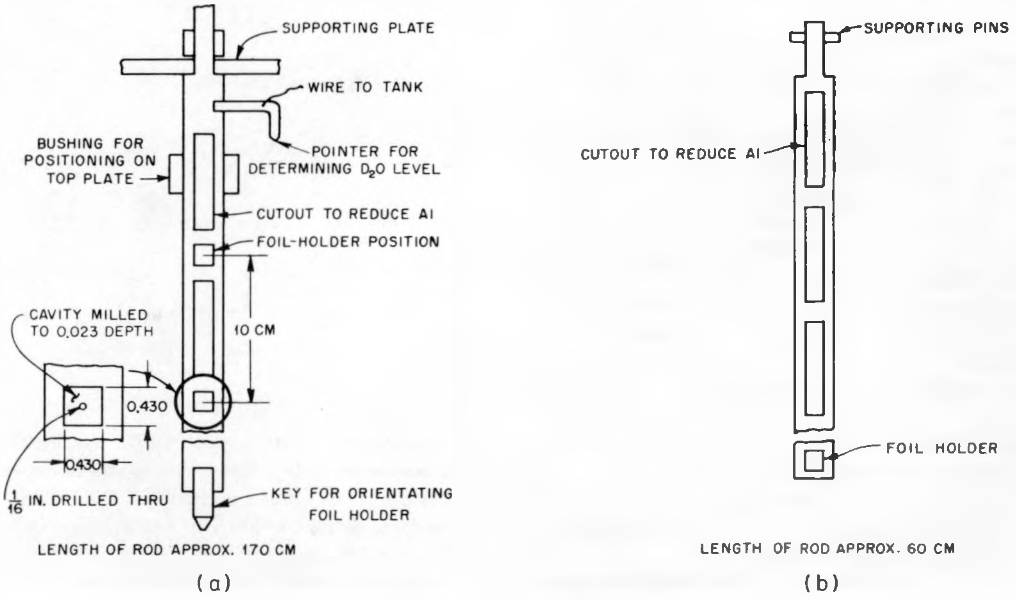


Fig. 5—Schematic diagram of the two types of foil holders used. (a) the foil holder used for determining axial and radial bucklings. (b) the foil holder used for flux traverses. The foil holders for flux traverses must be long enough to reach the relatively high flux available some distance below the surface of D_2O.

The foils are held vertically in the holders, and the z_i values are taken at the centers of the foils. This introduces no error since the average value of the hyperbolic sine over a given vertical interval introduces the same factor at each position. In the case of measurements of K the only restriction is that the holder be vertical. For radial measurements in a heterogeneous system corresponding lattice positions must be used.

The indium foils are counted by thin-wall aluminum Geiger tubes which have had previous dead-time calibration. The dead time is determined by least-squares fitting of the data obtained by following the decay of a very active indium foil. In this case, activation sufficient to require a 2 to 3 per cent dead-time correction is obtained initially. The indium mean life is considered to be known as $\tau = 78.35$ min from Wattenberg's measurements.[5]

Each foil is counted on four separate counters with reproducible geometry. Thus four foils can be counted simultaneously. In order to simplify computations of saturated activities, a single switch controls all four counters. The purpose of having four counters is to make sure that a defective counter does not invalidate a run, as well as to serve as a cross check on possible physical damage to the foils. It has been found, in fact, that the ratios of saturated activities between counters give an immediate indication of errors due to defective counters, damaged foils, or poor positioning of foils, either in the exponential tank or in the counter. Each counter has a separate uranium standard and a separate foil holder which remain with it. The counters are enclosed in lead, giving a background of approximately 30 counts/min. Backgrounds and standards are run several times daily. If air conditioning is not available, the counters must be protected against moisture. Each foil is counted for 10,000 counts in each of the four counters to obtain a probable error of ½ per cent.

EXPERIMENTAL PROCEDURES

The foils are punched from spectroscopically pure indium, and identification numbers are scratched on each foil. They are then weighed to the nearest ten-thousandth of a gram, and a set is made of those foils which weigh within ½ per cent of each other. This set is then calibrated by exposure in a standard reactor.

DECLASSIFIED

Each foil is irradiated in the same slot of the standard reactor and counted in each of the four counters to give ½ per cent accuracy. It has been found that foils are sufficiently uniform so that calibration in a standard reactor is unnecessary. The weights obtained serve to give the ½ per cent accuracy. In fact, if weight corrections are included, no foils need be eliminated. An error distribution function is obtained if the foils are calibrated with a standard reactor.

It has been found that good results, within 1 per cent for the Laplacian, can be obtained with about eight foils for an axial measurement and six to eleven foils for a radial measurement. To increase the number of radial measurements per exposure, two or three different heights are used at each run. In some previous exponentials it was found that the effective radius varied with the height of the measurement; however, we have been unable to observe this effect.

For flux traverses as many as 60 positions in a cell have been measured using a monitoring foil for normalization.

Once the method of analysis has been established and the equipment has been checked, it has been found that about 45 foils may be irradiated and counted easily within an 8-hr working day. Thus as many as five or six axial runs and two complete diametrical runs at two separate heights, the equivalent of about eight radial runs, may be done without excessive strain by a team consisting of one computor, one counter, one reactor operator, and three loaders. The loaders' job includes loading foil holders, placing and removing holders from tank, unloading foils, and supervising the experiment.

With this setup the computer will soon become overloaded; however, interruptions in the routine when the lattices are changed permit a computer, working steadily, to just about keep up with the accumulation of data.

All measurements except radials are done three times. Radial measurements are done a sufficient number of times to give good statistics on the effective radius. As will be seen below, what constitutes good statistics depends upon the characteristics of the material under investigation and the properties to be measured.

There are several methods for using an exponential experiment to determine the diffusion coefficient of a material. Asymptotic transport theory shows that the diffusion coefficient, D, is related to the extrapolation distance d by d = 2.13D. Thus, if one measures κ and fits the observed axial flux to the function A sinh κ (t − z), the extrapolation distance may be determined from the fitted results. A better method is to use the relation $L^2 = D/\Sigma_a$, where Σ_a is the macroscopic absorption cross section. In the case of cylindrical geometry Eq. 3 holds. L^2 may be determined by exponential measurements of κ and R. If it is possible to change Σ_a radically without producing an appreciable change in D, two observations are obtained conforming to

$$\frac{1}{L_1^2} = \frac{\Sigma_{a_1}}{D}, \qquad \frac{1}{L_2^2} = \frac{\Sigma_{a_2}}{D} \tag{29}$$

Taking the difference gives

$$\frac{1}{L_1^2} - \frac{1}{L_2^2} = \frac{1}{D}(\Sigma_{a_1} - \Sigma_{a_2}) \tag{30}$$

Since D has not changed appreciably, R^2 is unchanged so that

$$L_1^{-2} - L_2^{-2} = \kappa_1^2 - \kappa_2^2 \tag{31}$$

$$D = \frac{\Sigma_{a_1} - \Sigma_{a_2}}{\kappa_1^2 - \kappa_2^2} \tag{32}$$

A measurement of this type can be made, for example, with boron in D_2O. The scattering cross section of D_2O is so high that the addition of the relatively minor amounts of boron needed to make large changes in Σ_a of the mixture produces only small changes in D.

L^2 of any mixture is directly determined from axial and radial flux measurements and the use of Eq. 3.

On the other hand, if D is known from such measurements, Σ_a may be determined from $L^2 = D/\Sigma_a$. More accurate determination of Σ_a is possible by using Eq. 32 with a known D since this equation eliminates errors in R. An example of this is an experiment soon to be performed at Argonne to determine the proton absorption cross section. A series of measurements of L^2 will be made with various concentrations of H in D_2O. These will be compared with similar measurements using boron in D_2O, and the absorption cross section of H relative to the absorption cross section of boron will be determined. In order to avoid contaminating the D_2O with H, a chemical which does not exchange H with D will be introduced.

While the constants referred to above are those of a homogeneous mixture, they are applicable to heterogeneous systems if proper corrections are applied. The heterogeneous system is most frequently computed as a homogeneous system using a flux-weighted average for the constants. By performing a series of flux traverses throughout the cell of a heterogeneous lattice, the proper weighting factors are found.

Although several of the experiments mentioned above, in particular, determination of D and Σ_a, have not yet been completed, a number of the experiments mentioned have been analyzed and results have been obtained which illustrate the exponential technique.

DECLASSIFIED

The complete results for a typical lattice are shown below.

A series of 16 radial measurements were completed and fitted to the J_0 function with the following results:

Effective radius, cm

78.05	77.98	77.51	77.73
77.97	78.00	77.92	77.52
77.94	77.75	77.89	79.10
78.15	77.68	78.17	79.10

From these 16 runs, giving low weight to values far from the mean, the effective radius was found to be 77.96 ± 0.06 cm.*

The vertical relaxation constant was determined from the average of the three runs 0.00845, 0.00857, and 0.00858 to be 0.00853 ± 0.00005/cm. It will be seen that for the determination of B^2 the error in κ is relatively unimportant for small κ. The resulting buckling of the lattice (in cm^{-2}) is

$$B^2 = B_r^2 - \kappa^2 = \left[\frac{2.4048}{77.96(1 \pm 0.0008)}\right]^2 - [0.00853(1 \pm 0.006)]^2$$

$$= [952(1 \pm 0.0016) - 73(1 \pm 0.012)]10^{-6}$$

$$= \left[(952 - 73) \pm (1.5^2 + 0.9^2)^{1/2}\right] \times 10^{-6} = (879 \pm 2) \times 10^{-6}$$

The L^2 of the system was obtained in the following way: A set of 2½ per cent mercury in lead alloy rods was made. The macroscopic absorption and scattering cross sections were within 10 per cent of the values for uranium, and the dimensions were those of the uranium rods. L^2 was determined by performing an exponential experiment with these rods replacing the uranium. At the same time a diffusion-theory calculation for L^2 was made. An empirical correction factor was thus found between observed value and theory, and this correction was applied to the diffusion-theory calculation of L^2 for uranium rods. By this means, we arrived at a value of $L^2 = 143(1 \pm 0.05)$. Here the 5 per cent error is an estimate of the uncertainties due to errors in cross sections, neutron temperature, and theoretical naiveté. Assuming τ_f and τ_e known, K can then be found from a three-group calculation to be

$$K = (1 + L^2B^2)(1 + \tau_f B^2)\, e^{\tau_e B^2}$$

where $\tau_f = 48\ cm^2$ and $\tau_e = 79\ cm^2$

$$K = \{1 + [143(1 \pm 0.05)][879(1 \pm 0.002)10^{-6}]\}$$
$$\{1 + 48[879(1 \pm 0.002)10^{-6}]\} \exp \{79[879(1 \pm 0.002)10^{-6}]\}$$

or

$$K = 1.258 \pm 0.008$$

The errors in the buckling arise from two factors. The lack of precision of the radial measurement represents a constant absolute error in B^2 for all experiments performed in a given tank; the axial relaxation length κ may be shown to have a constant expected error for all κ, so long as the distances over which the relaxation is measured are kept constant. Hence, the error in B^2 is $\delta B^2 + 2\kappa\,\delta\kappa$ and varies only slowly with κ; B^2 is known within approximately a constant absolute error.

Because this error is small, the precision of K − 1 is highly dependent on the precision of M^2 and only secondarily on B^2, down to $K \doteq 1.02$, for the sort of experiments performed here.

APPENDIX A

Detailed Theory of Flux Harmonics

The eigenfunction given by Eq. 2 is the leading term of an infinite number of solutions, each satisfying the boundary conditions that flux vanish at radius R and height t.

The first problem we consider is that of the radial distribution of source neutrons which travel through the system. We may write the complete solution of the diffusion equation in a cylindrically symmetrical system as a Fourier-Bessel expansion in the radial coordinate

$$\phi = \sum_{i=1}^{\infty} J_0\left(\frac{j_{0i} r}{R}\right) f_i(z) \qquad (33)$$

where j_{0i} is the i root of the Bessel function† of order n.

Substituting Eq. 33 into the diffusion equation we obtain

$$-D \frac{j_{0i}^2}{R^2} f_i(z) + Df_i''(z) - \Sigma_a f_i(z) = 0 \qquad (34)$$

The solutions of Eq. 34 are

$$f_i(z) = A_i \exp\left[z\sqrt{\frac{1}{L^2} + \left(\frac{j_{0i}}{R}\right)^2}\right] + C_i \exp\left[-z\sqrt{\frac{1}{L^2} + \left(\frac{j_{0i}}{R}\right)^2}\right] \qquad (35)$$

---

*Unless otherwise stated, errors listed are probable errors.

†The first three roots of $J_0(x)$ are x = 2.405, 5.520, and 8.654.

DECLASSIFIED

Since the neutron-source flux is being continually attenuated, the derivative of this flux must always be negative. Also, the flux itself must always be positive. Applying these conditions at z = t, the thickness of the region under consideration, the relations obtained from Eq. 35 are

$$\begin{aligned} A_i &< C_i \exp\left[-2t\sqrt{\frac{1}{L^2}+\left(\frac{j_{0i}}{R}\right)^2}\right] \\ -A_i &< C_i \exp\left[-2t\sqrt{\frac{1}{L^2}+\left(\frac{j_{0i}}{R}\right)^2}\right] \end{aligned} \tag{36}$$

Solving Eq. 36, we may easily show that C_i is positive and that therefore

$$|A_i| \leq C_i \exp\left[-2t\sqrt{\frac{1}{L^2}+\left(\frac{j_{0i}}{R}\right)^2}\right]$$

hence the general characteristics of the attenuation may be determined by inspecting only the negative exponential term in Eq. 35.

Two positions of mismatch occur. They are at the junctions of the thermal column with the pedestal and the junctions of the pedestal with the tank. From Eq. 35 it may be seen that higher harmonics (solutions for i > 1) are damped out more rapidly than the fundamental (i = 1). Hence, if the thermal column or the pedestal is long enough, only the fundamental exists far from the source. In fact, the pedestal merely serves as a cheap method of achieving the above damping. If lattice materials were less expensive, the same effect could be achieved with a taller lattice by making measurements sufficiently high in the lattice so that harmonics have disappeared. We assume, therefore, that the thermal column is sufficiently long so that at the base of the pedestal we can neglect all harmonics and write

$$\phi(z = 0) = AJ_0\,\frac{j_{01}r}{R_0} \tag{37}$$

where R_0 is the extrapolated radius of the thermal column.

Equation 37 assumes the thermal column to be a cylinder of radius R_0. If you have a square thermal column and a round pedestal, the process of determining the radial harmonic coefficients is similar to that of matching two cylinders of different radii. The square column is first replaced by a cylinder of equivalent diffusion characteristics. The κ^2 in a square pedestal is

$$\kappa^2 = 2\left(\frac{\pi}{b}\right)^2 + \frac{1}{L^2} \tag{38}$$

where b is the length of a side; hence

$$R_0 = \frac{j_{01}b}{\pi\sqrt{2}} \tag{39}$$

In order to examine the perturbations introduced we shall use only the negative exponential terms in Eq. 35. This procedure is justified by the argument of Eq. 36.

The fact that R_0, the equivalent thermal-column radius, is different from R_1, the pedestal radius, introduces harmonics in the pedestal. We may expand

$$\phi(z = 0) = AJ_0\left(\frac{j_{01}r}{R_0}\right) = \sum_i A_iJ_0\left(\frac{j_{0i}r}{R_1}\right) \tag{40}$$

Using the orthogonality of the Bessel functions in the right-hand side of Eq. 40, we multiply both sides by $J_0\left(\frac{j_{0k}r}{R_1}\right)$ r dr and integrate from 0 to R_1

$$A_k = \frac{2}{j_{0k}J_1(j_{0k})}\left[\frac{J_0\left(\frac{j_{01}R_1}{R_0}\right)}{1-\frac{j_{01}^2}{j_{0k}^2}\,\frac{R_1^2}{R_0^2}}\right] \tag{41}$$

An examination of the A_k permits a determination of the relative radial harmonic content at the base of the pedestal. For any of the modes the axial relaxation constants are obtained from

$$\kappa_i^2 = \frac{j_{0i}^2}{R_1^2} + \frac{1}{L^2} \tag{42}$$

For a good thermal column or pedestal $1/L^2 \ll (j_{0i}/R)^2$ and, since the ratio of the Bessel functions is of the order of unity, we may write

$$\frac{\phi_2}{\phi_1} = \frac{A_0}{A_1}\exp\left[\frac{(j_{02}-j_{01})}{R_1}z\right] = \frac{A_2}{A_1}e^{3.12z/R} \tag{43}$$

Higher harmonics are damped even more rapidly, and, with z = R, the pedestal can be considered black to all except the fundamental.

The matching of a square thermal column to a circular pedestal also introduces angle-dependent terms in cos 4nθ. We shall examine the solution for the terms n = 0 and n = 1 and observe how rapidly the angular terms are damped.

For n = 0, we have already shown that the lowest harmonic satisfying the boundary conditions is

$$\phi_0 = A_0J_0\left(\frac{j_{01}r}{R}\right)\exp\left[-z\sqrt{\frac{1}{L^2}+\left(\frac{j_{01}}{R}\right)^2}\right] \tag{44}$$

For n = 1, the corresponding lowest term is

$$\phi_1 = A_1 J_4\left(\frac{j_{41}r}{R}\right)\cos 4\theta \exp\left[-z\sqrt{\frac{1}{L^2}+\left(\frac{j_{41}}{R}\right)^2}\right] \quad (45)$$

where j_{41} is the first root of the Bessel function of order 4. Then, omitting the Bessel functions as before and remembering that $1/L^2 \ll (j_{rs}/R)^2$, we get

$$\frac{\phi_1}{\phi_0} \doteq \cos 4\theta \left\{\frac{A_1}{A_0}\exp\left[-\frac{(j_{41}-j_{01})z}{R}\right]\right\}$$

$$\leqslant \frac{A_1}{A_0}\exp\left(-\frac{5.19z}{R}\right) \quad (46)$$

A_1/A_0 is the relative angular harmonic content at the base of the pedestal. From Eq. 46, if $z = R$, this harmonic content is less than 1 per cent of that present at the base. Here again the damping is so rapid that the pedestal is effectively black for higher harmonics.

APPENDIX B

Multigroup Effect on Neutron Flux in the Lattice

In the previous sections we have considered the tank as infinite in determining the properties of perturbations near the bottom of the tank. We shall now assume that measurements are made sufficiently far from the tank bottom so that these harmonic perturbations may be ignored.

In measurements on nonmultiplying lattices, the only other perturbation encountered is that caused by the finite height of the tank. This perturbation requires the use of the function $\sinh \kappa(t-z)$ in place of $e^{-\kappa z}$ wherever it appears, t being the (extrapolated) elevation of the top of the system.

In dealing with multiplying lattices the variation of neutron spectrum throughout the length of the tank must be considered. Inasmuch as detection is energy sensitive, our measurements are meaningful only in regions of constant spectrum. These regions are best checked by Cd ratio measurements on the foils, but the qualitative argument given below is useful in estimating their location.

We adopt the two-group theory for a qualitative picture. The equations are.

$$\nabla^2\phi_f - \frac{\phi_f}{\tau} + \frac{K\Sigma_s\phi_s}{D_f} = 0$$

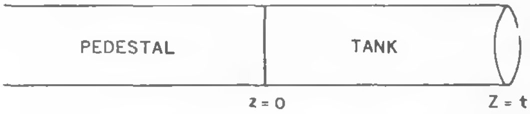
$$\nabla^2\phi_s - \frac{\phi_s}{L^2} + \frac{\Sigma_f\phi_f}{D_s} = 0 \quad (47)$$

where τ = the two-group neutron age
L^2 = thermal diffusion area
D_f = the fast diffusion coefficient
D_s = the thermal diffusion coefficient

$$\Sigma_f = \frac{D_f}{\tau}$$

$$\Sigma_s = \frac{D_s}{L^2} \quad (48)$$

The boundary conditions are that ϕ_f and $D_f(\partial\phi_f/\partial z)$ be continuous, ϕ_s and ϕ_f shall vanish at $z = t$, and ϕ_s be specified at the bottom of the tank ($z = 0$). This latter is, in effect, the inhomogeneous boundary condition required to take into account the presence of a driving current into the system. $\phi_f(-\infty) = 0$, corresponding to the source deep in the graphite being purely thermal.



Where the origin has been taken at the base of the tank and is positive into the tank, the solutions of the problem for the fast flux for the pedestal and tank, respectively, are

$$\phi_f = A \exp\left(z\sqrt{\frac{1}{\tau_c} + B_r^2}\right) \quad (49)$$

$$\phi_f = E \sinh k(t-z) + C \sinh m(t-z) \quad (50)$$

where τ_c = the neutron age in graphite
B_r^2 = the radial buckling or $(j_{01}/R)^2$
$k^2 = B_r^2 - \overline{k^2}$
$m^2 = \overline{m^2} + B_r^2$

The solutions for B^2 of the critical equation

$$K = (1 + L^2B^2)(1 + \tau B^2) \quad (51)$$

are $\overline{k^2}$ and $-\overline{m^2}$, where $\overline{k^2} < \overline{m^2}$.

The slow flux in the lattice is given by

$$\phi_s = S_1E \sinh k(t-z) + S_2C \sinh m(t-z) \quad (52)$$

where

$$S_1 = \frac{\Sigma_f}{\Sigma_s(1 + L^2k^2)}$$

$$S_2 = \frac{\Sigma_f}{\Sigma_s(1 - L^2m^2)} \quad (53)$$

Eliminating constants by using the boundary conditions of continuity of fast flux and current at the base of the tank and defining

$$\alpha \equiv \frac{D_c}{D_l}\sqrt{\frac{1}{\tau_c} + B_r^2} \quad (54)$$

DECLASSIFIED

where D_c and D_l are the fast diffusion coefficients in graphite and the lattice, respectively, we obtain for the ratio of thermal to fast flux in the lattice

$$\frac{\phi_s}{\phi_f} = S_1 \frac{1 - \frac{S_2}{S_1}\frac{G_1 G_3}{G_2 G_4}}{1 - \frac{G_1 G_3}{G_2 G_4}} \tag{55}$$

where $G_1 = \sinh m(t - z)$
$G_2 = \sinh k(t - z)$
$G_3 = \alpha \sinh kt + k \cosh kt$
$G_4 = \alpha \sinh mt + m \cosh mt$

For ϕ_s/ϕ_f to be reasonably constant there must exist a z_0 such that for $z > z_0$ the terms $t - z$ in Eq. 55 are practically constant. We assume t to be large enough so that $\sinh kt \doteq \cosh kt$, $\sinh mt \doteq \cosh mt$ and thereby obtain

$$\frac{\alpha + k}{\alpha + m}\, e^{-(m-k)z_0} < \delta \tag{56}$$

where δ is our criterion of constancy for ϕ_s/ϕ_f.

In general, $m \gg k$ and $m^2 = (1/L^2) + (1/\tau) + B_r^2$, as can be seen from the solutions of Eq. 51. Thus the requirement reduces to

$$\exp\left(-z_0\sqrt{\frac{1}{L^2} + \frac{1}{\tau} + B_r^2}\right) < \delta \tag{57}$$

REFERENCES

1. H. L. Anderson, B. Feld, G. Weil, and W. Zinn, Neutron Reproduction in a Lattice Uranium Oxide and Graphite Exponential Experiment, Report C-20.
2. A. V. Masket and H. R. Kroeger, A Guide with Abstracts to Critical Masses, Laplacians, and Multiplication Factors (Part I), Report ORNL-112, Jan. 17, 1949.
3. F. L. Friedman and A. Wattenberg, The Slowing Down of Neutrons in Heavy Water, Report CP-3453. (This value is corrected for the age from indium resonance to thermal energies according to the formula given on p. 8, Chap. IV, Part E, Project Handbook, Report CL-697.)
4. Project Handbook, Report CL-697, Chap. IV, Part E, p. 11.
5. B. Russel and A. Wattenberg, The Half Life of Indium, Report CP-3305, Oct. 19, 1945.

March 1951

A HIGH-TEMPERATURE REACTOR FOR POWER BREEDER APPLICATION

By SIDNEY SIEGEL

Atomic Energy Research Department
North American Aviation, Inc.
Downey, California

Report NAA-SR-147 (Del.)

ABSTRACT

A particular example, a graphite core homogeneously impregnated with U^{233} as the carbide, is shown to have attractive possibilities as a power breeder. A liquid bismuth – cooled design is discussed with a doubling time of approximately 300 days. Of prime importance for such an application is the chemical-processing cycle, and means whereby this may be reduced in duration are described, which apply particularly to the type of reactor fuel structure under consideration.

INTRODUCTION

North American Aviation, Inc. (NAA), has been investigating the properties of graphite and other refractory materials at temperatures up to 2000°C and reactors and power plants which might be designed to operate at such elevated temperatures. This program has reached a stage where a review of the utility and the feasibility of attaining its objectives is appropriate; view is presented in this article.

A high-temperature reactor and its associated power plant may make it possible to achieve the following objectives:

1. High-thermal-efficiency stationary power plants for production of electrical power
2. High power density reactors which also satisfy the nuclear criteria for breeding, making a short doubling time possible

The reactor which has received most specific study has a graphite core homogeneously impregnated with enriched fuel, either U^{235}, or U^{233} for the power breeder. The reactor operates on neutrons of thermal energies and is cooled by either high-pressure He gas or a suitable liquid metal; the metals Bi, Pb, Mg, and Sn are possibilities.

The results of the studies, reported in further detail in subsequent sections of this article, may be summarized briefly here. The stationary high-efficiency power plant has questionable value as a competitor with conventional hydrocarbon plants unless it is subsidized by its by-products, for example, plutonium production.

The possibilities of this reactor as a power breeder appear good. Operation at high temperature has as concomitants high specific power and high thermal efficiency for the associated power plant. Since the high-cross-section poisons produced in fission will be released from the hot porous graphite core into the coolant and can be removed continually from the cooling system, the breeding gain can be made high. No processing of a metallurgical nature is required in the refabrication of the core, and, consequently, the total inventory of fuel is only a few times that present in the reactor. This combination of features leads to a doubling time of the order of 300 days, quite attrac-

TID 148

DECLASSIFIED

tive for a breeding cycle; it is also of importance for a naval reactor, in keeping to a minimum the total inventory of fuel required for continuous operation of the vessel and in reducing the severity of control problems having their origin in fission-product-neutron absorbers.

While the original emphasis in this program was on the highest attainable temperature, in order to maximize thermal efficiency, more recent studies have indicated that a reactor operating at lower temperatures may be of equal interest. For the power breeder application, in particular, the lowest temperature at which it is possible to achieve such necessary operating conditions as diffusion of fission-product poisons out of the core and annealing of radiation damage will probably be the most realistically desirable operating temperature.

HIGH-EFFICIENCY STATIONARY POWER PLANTS

The relation between maximum operating temperature and thermal efficiency of power plants has already received general study,[1] and the results are given in Report NAA-SR-63. It is concluded there that a compounded Na vapor – Hg vapor – steam system operating with a maximum temperature of 1800°C can have a thermal efficiency of 50 per cent, about twice that of modern steam plants. This conclusion is predicated, of course, on the assumption that it will be possible to develop high-efficiency components for the power system and also a nuclear reactor capable of delivering its heat output near 2000°C.

Under what circumstances is a high-thermal-efficiency power plant worth while? In hydrocarbon-fueled plants designed solely for the production of commercial power the only requirement is the minimum unit power cost. In such plants, where fuel costs are of the order of one-half (or more) of the total production cost, extensive experience has already demonstrated the worth, in reduced over-all cost of power, of adding to existing plants "topping" turbines and high-pressure boilers operating at higher maximum temperatures. A study of the operations of a large number of existing steam power plants reveals the data shown in Fig. 1, in which the over-all plant efficiency is plotted against steam temperature in the plant. The economic utility of these high-temperature steam plants arises not only from the reduced fuel costs, which Fig. 1 implies, but also from other reductions in operating cost, as shown in Fig. 2, where operating costs, exclusive of fuel, are plotted against steam temperature. It should be pointed out, however, that steam temperature is not a completely independent variable because the more modern plants operating at higher temperatures have a greater degree of mechanization and automatic control, with accompanying reduced labor costs, which are not directly tied to plant temperature.

The capital cost of these higher temperature plants is not, however, significantly affected by going to high-temperature operation. The cost per installed kilowatt-hour capacity is plotted against steam temperature in Fig. 3. These plants were built at different times; therefore the plant cost is reduced to a single base by the use of price indexes. It is apparent that no decrease in capital investment arises from the utilization of high temperatures. It is evident, therefore, that the trend toward higher operating temperature in modern hydrocarbon-fuel-fired steam power plants has led to reduced fuel and other production expenses, but not to reduced capital investment.

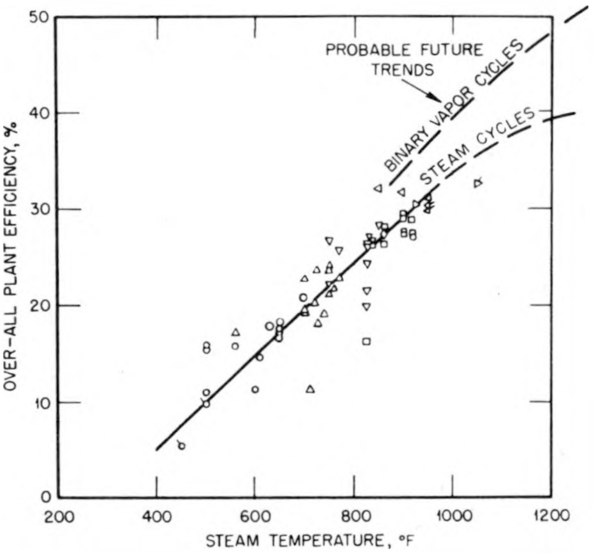


Fig. 1 — Over-all efficiencies of steam-electric plants. Pressure (psig): ○, 101 to 300; △, 301 to 500; ▽, 501 to 700; □, 701 to 900; ◊, 901 to 1100; ◁, 1101 to 1300; ▷, 1301 to 1500. Data from Federal Power Commission, Report S-72 (1947). ○, are from "Combustion," January 1951, p. 40. ▷, are from "Electrical World," Apr. 24, 1950.

All studies to date have indicated that a nuclear power plant operated for power alone cannot, in general, now compete economically with hydrocarbon-fueled power plants. However, if a portion of the operating cost is borne by the value of by-products, e.g., plutonium, then it does appear likely that such a multipurpose system can be economically justified. Since the plutonium production costs from a high-temperature (near 2000°C) reactor and the operating costs of the associated unconventional power plant will probably be higher than these costs in the range of conventional power plant practice (near 500°C), it appears

DECLASSIFIED

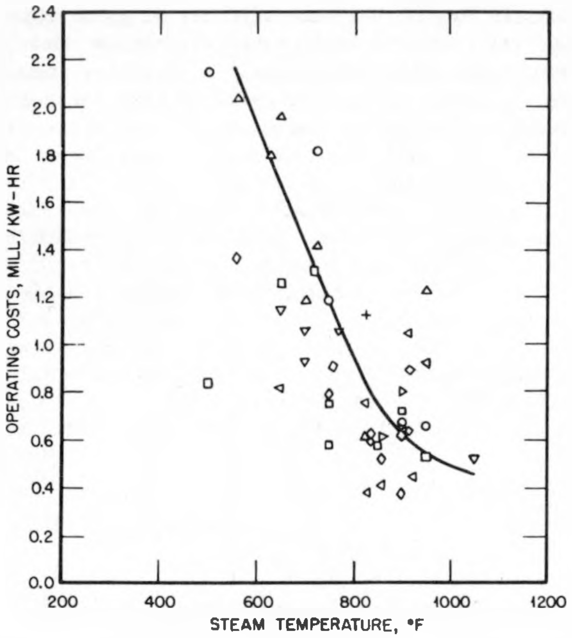


Fig. 2—Operating costs, not including fuel, of steam-electric plants. Load factor (%): +, below 35; ○, 36 to 45; △, 46 to 55; ▽, 56 to 65; □, 66 to 75; ◇, 76 to 85; ◁, 86 to 95; ▷, 96 and up. Data mainly from Federal Power Commission, Report S-72 (1947). Plants smaller than 20 megawatts omitted.

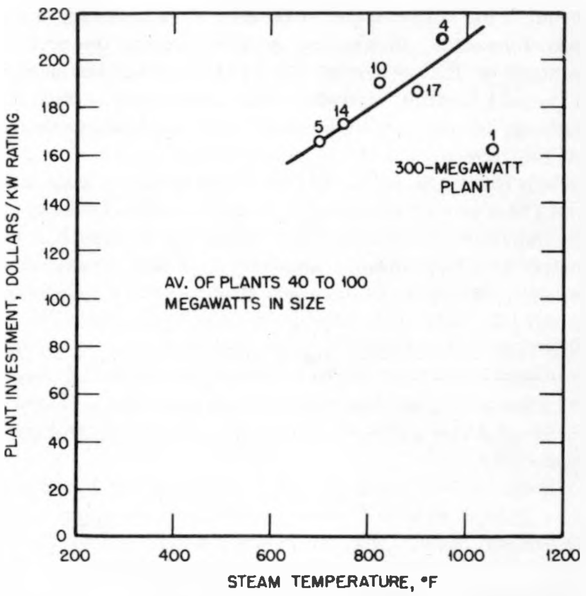


Fig. 3—Construction cost of steam-electric plants. All costs corrected for the wholesale price index at the time of construction, referred to 1947 as datum. Data from Federal Power Commission, Report S-72 and from "Electrical World," Apr. 24, 1950. Numbers beside points indicate the number of plants represented by each point.

that a plant operating near 2000°C cannot be justified at present. In fact, because of the necessity to keep the Pu production cost low, the optimum temperature for such a multipurpose reactor may be even lower than 500°C.

Our conclusion is, therefore, that while a high-temperature power plant will maximize thermal efficiency and conversion of nuclear fuel to useful power, it cannot be justified so long as such a plant must be subsidized by plutonium production and so long as the cost of such production is increased by high-temperature operation.

POWER BREEDER REACTOR

An important criterion for a power breeder reactor is its doubling time, the time in which the initial inventory of fissionable material is doubled. This time is given by

$$t_d = \frac{0.69 \times 10^3 \text{ days}}{w(1+\alpha)(\eta - 2 - L)} \qquad (1)$$

where w is the specific power in megawatts per kilogram of fuel invested in the reactor and the fuel processing plant; L is the fraction of neutrons lost per fission by parasitic absorption, useless leakage, and equivalent loss of product or fuel in the chemical-processing cycle; $1 + \alpha$ is the ratio of capture to fission cross section for the fuel material. For U^{233}, $\eta = 2.35$ for neutrons of thermal energy; since L can probably be kept near 0.2 or less, a Th^{232}-U^{233} breeding cycle is possible.

The specific power w_r in the reactor is related to the fractional burn-up B during the life of a core and to the time t_r required for this burn-up by the equation

$$w_r = \frac{10^3 B}{(t_r)(1+\alpha)} \text{ megawatts/kg} \qquad (2)$$

where t_r is expressed in days. The specific power w in the entire reactor complex, including the fuel tied up in chemical reprocessing of spent cores, is given by

$$w = \frac{10^3 B'}{(t_r + t_p)(1+\alpha)} \qquad (3)$$

where t_p is the time, in days, required to reprocess completely a spent core and prepare it for reinsertion into the reactor.

The reactor which is being most actively studied at NAA for the power breeder application has a core

DECLASSIFIED

made from conventional reactor-grade graphite impregnated, by chemical means which will be described later, with U^{233} as the carbide. The core has the shape of a right circular cylinder of the order of 1.5 meters high by 1.5 meters in diameter. It has coolant channels arranged parallel to its axis, through which high-pressure He gas or a suitable liquid metal is pumped. The chemical-processing cycle for a core of this type is particularly simple, and it appears feasible to achieve a processing cycle time t_p of four days. The relative decrease in doubling time becomes progressively smaller and less worth while when $t_r \ll t_p$, therefore, we assume t_p to be two days. For reasons arising partly from control problems and partly from the possibility of radiation damage to the core material, a reasonable value for the fractional burn-up B is probably 0.15.

Using these values of B, t_r, and t_p in Eq. 2, a specific power w in the entire system is obtained, w = 22 megawatts/kg. For the reactor alone,

$$w_r = w\left(1 + \frac{t_p}{t_r}\right)$$

$$= 67 \text{ megawatts/kg}$$

An important advantage of this reactor core design is the fact that the high-cross-section poisons formed in fission will rapidly diffuse out of the core and can be removed from the system in a continuous fashion. It is this fact which makes neutron losses of 0.2, or less, realistic; the situation is similar to that discussed for the homogeneous aqueous reactor in Report ORNL-855. The doubling time t_d may now be estimated from Eq. 1, and the assumption that the neutron losses can be kept at L = 0.2

$$t_d = \frac{0.69 \times 10^3}{(22)\,(1.1)\,(0.15)} \text{ days}$$

$$= 190 \text{ days}$$

The doubling time here estimated is that which the system attains when it is in steady-state operation, after transient conditions which have their origin in the relatively long (compared to the time the core spends in the system) half life of Pa^{233}. The transient period during which the reactor would have to operate on U^{235} as the fuel, until enough thorium has been converted to U^{233} to shift over to a true breeding cycle, has also been neglected. This system, in common with any other 23 breeder cycle of short doubling time, will always have tied up in decaying protactinium a considerable amount of latent fuel material, so that the concept of doubling time becomes somewhat ambiguous. The doubling time here is that required to double the amount of fuel in the entire system in steady-state operation with a fictitious value of $\tau_{1/2}(Pa^{233}) = 0$. The long half life of protactinium leads to a delayed fuel production, but the fuel is always available in latent form; it is not inherently tied into the operating system in the same sense that the fuel held up in chemical processing is, and it is not taken into account in computing the specific power for the entire complex. These remarks apply, of course, only to steady-state operation. Since the steady state is achieved in about one year under the conditions considered here, this is not an unreasonable premise.

Thus, a reactor and processing complex capable of attaining a specific power of 67 megawatts/kg in the reactor and having a total cycle time of six days has attractive possibilities as a breeder, and our studies indicate that such conditions probably can be attained in a homogeneously impregnated graphite thermal reactor.

HOMOGENEOUS ENRICHED FUEL IMPREGNATED GRAPHITE REACTOR

Physical Properties of Graphite Impregnated with Uranium

A considerable amount of data on the physical and mechanical properties of graphite at temperatures up to, and exceeding, 2000°C has been accumulated and has been summarized recently.[3] The properties of importance, such as strength, creep rate, and thermal conductivity, appear adequate for the contemplated conditions of operation of the reactor; this statement is predicated on the assumption that the properties of graphite impregnated with about 10 mg/cm² of UC_2 are not significantly different from those of pure graphite. On this point there is little experimental information, but recent experiments indicate that impregnation with 10 mg/cm³ of uranium does not change the tensile strength. It is clear, however, that much more extensive information on the properties of impregnated graphite is required. In particular, the effect of radiation on the thermal conductivity of this material at operating temperatures in the neighborhood of 1500°C must be determined. Hunter's[4] experiments near 800°C indicate a serious deterioration of thermal conductivity, while the "neutron annealing" experiments on Hanford graphite at 350°C would lead to the conclusion that high-temperature operation would result in little reduction of thermal conductivity by radiation. This uncertainty must be resolved in order to determine how seriously the design will be affected by the phenomenon.

Specific Power, Breeding Gain, and Doubling Time

1. Helium Cooling. Neutron-physics, heat-transfer, thermal-stress calculations, etc., have been made on a reactor in which the core is a right circular

UNCLASSIFIED

cylinder 4 ft in diameter by 4 ft high, impregnated with uranium in the form of the carbide. The fractional void volume (1 − S) equals ¼, occupied by cylindrical cooling channels, ¼ in. in diameter, parallel to the axis of the cylinder. A two-group-theory calculation for this core surrounded by a graphite reflector and thorium breeding blanket indicates a critical mass near 20 kg at 2000°C.

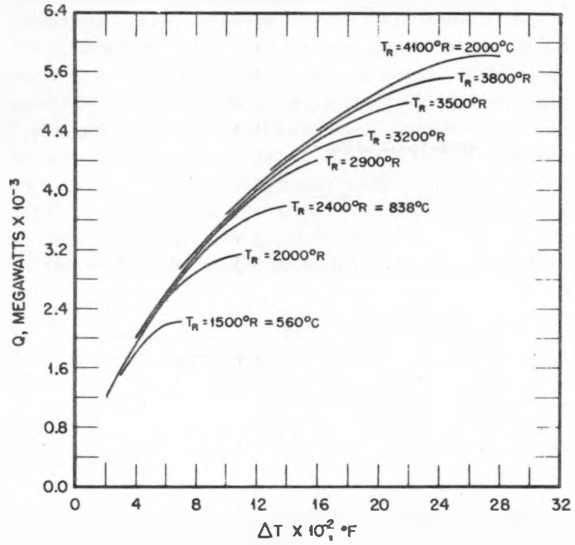


Fig. 4 — Total Q as a function of ΔT. Gas, He; P_1, 2000 psi; T_1, 700°R = 112°C; M_2, 0.459.

The coolant conditions considered were inlet helium pressure, 2000 psi; inlet temperature, 115°C; and exit Mach No., 0.46. Curves of the total power Q in the reactor, for various reactor wall temperatures, are plotted in Fig. 4 as functions of the temperature rise of the gas. Calculations were also made on the pumping power W required under these conditions, and curves showing the fraction of total heat required for pumping power, for various values of power density δ, are plotted against reactor temperature in Fig. 5.

If we assume that the pump machinery has an efficiency of 50 per cent and the reactor power plant has an efficiency of 33 per cent, then, if $W/Q = 1/6$, all the power output of the reactor goes into pumping; if $W/Q < 1/6$, some power is left over for other purposes. The curves of Fig. 5 indicate that with a specific power of 70 megawatts/kg, which for the reactor core size being considered requires a power density $\delta \cong 1$ kw/cm³, the reactor operating temperature must be near 1500°C and even there $W/Q = 1/6$. It is apparent that such a reactor system may still be a power burden rather than a power producer if the power plant efficiency is as low as 33 per cent, about the maximum attainable with conventional steam plants. If we wish to produce enough power to at least operate the pumps, the reactor power plant must have an efficiency of at least

$$e = \frac{W/Q}{f} \tag{4}$$

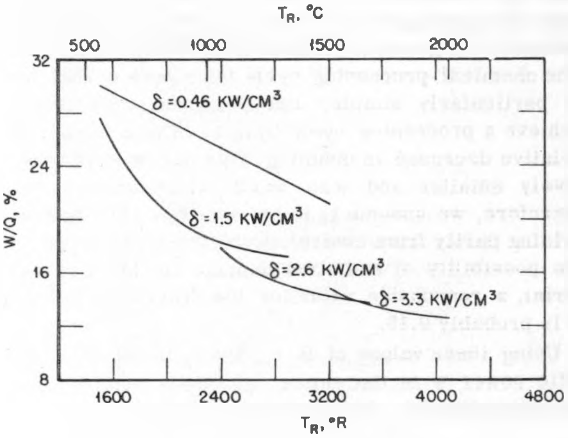


Fig. 5 — W/Q vs. reactor temperature.

where f is the mechanical efficiency of the pumping machinery.

For the reactor to produce net power in addition to that required to pump the coolant, the power plant must be significantly greater than 33 per cent. This can be achieved by operating the reactor at a high temperature (near 2000°C) and utilizing unconventional power plants, for example, the type of compounded Na vapor–Hg vapor–steam plants discussed in Report NAA-SR-63.

Under the proposed operating conditions, namely 2000°C with a specific power of ~70 megawatts/kg, and with the core structure described, the maximum thermal stresses in the core may be estimated. The maximum temperature rise in the graphite webs between the coolant passages is 500°C; the thermal stress is

$$\sigma = C\alpha E\,\Delta T$$

where α is the coefficient of expansion, E is the elastic modulus, and, for the shape under consideration here, C is about ¼. For graphite at 2000°C, reasonable values[3] appear to be $\alpha = 5 \times 10^{-6}$ and $E = 1.5 \times 10^{6}$ psi. Hence, the maximum local thermal stress at 75 megawatts/kg is

152
DECLASSIFIED

$$\sigma = \tfrac{1}{4} \times 5 \times 10^{-6} \times 1.5 \times 10^{6} \times 500°\text{C}$$
$$\cong 1000 \text{ psi}$$

At 2000°C and 1000 psi stress, the creep rate is less than 10^{-5} per hr. The short-time tensile strength at 2000°C is about 3600 psi, so both the creep rate and the thermal-stress level are acceptable under the conditions considered.

Table 2—Axial-flow Helium Compressor

Inlet temperature, °C	115
Inlet pressure, atm	83
Exit pressure, atm	136
Number of stages	25
Rotative speed, rpm	4,000
Power requirement, hp	500,000
Diameter, ft	3
Length, ft	15

These considerations indicate that, with high-pressure helium as the coolant, heat-transfer rates adequate to permit a specific power of 70 megawatts/kg, in a structure which appears mechanically reasonable and in which thermal stresses are satisfactorily low, can be achieved. The pumping power required is quite large, however, and, in fact, the design of the helium compressor will be a major engineering development problem. A preliminary analysis of the compressor required indicates that an axial-flow machine can be made to meet the needs of the system. The characteristics of such a machine are given in Table 2.

In the reactor core the only materials present are graphite and U^{233}, in about the ratio of 2000 carbon atoms to 1 atom of 23. The neutron loss per fission due to absorption in the graphite is $l_c = 0.02$ for such a composition. In Table 3 values of the total neutron losses, the breeding gain, and the doubling time for a system specific power of 22 megawatts/kg are tabulated for three different values of l_0, the neutron losses due to causes other than graphite absorption, e.g., useless leakage, fission-product-poison absorption, chemical-processing losses. Since it is not unreasonable to assume that l_0 can be as low as 0.15, particularly since the major fraction of the fission-product poisons will be continuously removed from the core during operation, an exceptionally favorable doubling time of 160 days appears achievable. A major problem is the development of a compressor capable of pumping the volume of gas necessary to cool the reactor.

Other possible core designs, predicated on cooling by diffusion through the pores of a graphite plate structure rather than by gas flow through parallel axial holes, may lead to better heat-transfer conditions, lower values of W/Q, but with accompanying difficulties in reactor arrangement. Such possibilities have been studied at Battelle Memorial Institute[5] and will be examined further for the present application.

2. Liquid Metal Cooling. Since the gas compressor for the helium-cooled reactor appears to be a monumental piece of equipment, attention was given to a series of reactors in which the coolant is a suitable liquid metal. Preliminary corrosion tests indicate that graphite behaves satisfactorily in contact with liquid Bi, Pb, Mg, and Sn at the contemplated operating temperature, near 1500°C.

Table 3—Neutron Losses in Helium-cooled Reactor

	$l_0 = 0.05$	$l_0 = 0.10$	$l_0 = 0.15$
l_c	0.02	0.02	0.02
$L = l_0 + l_c$	0.07	0.12	0.17
Breeding gain ($\eta - 2 - L$)	0.28	0.23	0.18
t_d, days	100	125	160

With liquid metals the pumping power is very low, and it is possible to use higher values of the solidity S than 0.75, the case considered for the helium-cooled reactor. Heat-transfer computations were carried out on two typical core arrangements (Fig. 6). In case (a) the graphite core is homogeneously impregnated with fuel, the metal coolant flowing in axial holes; in case (b) only the tube is impregnated with fuel, and the coolant flows in both the annulus and the hole. In each case an average power density throughout the core of 750 watts/cm³ and a maximum thermal stress of 2000 psi anywhere in the graphite at operating temperature were specified. In Table 4 values of hole diameters, maximum temperature rise, and other relevant parameters are given for these heat-transfer conditions with a solidity of 0.9 and 0.8. It is evident that a power density of 750 watts/cm³ is quite reasonable.

With 10 per cent of the reactor core occupied by coolant passages and the additional likelihood that the porous nature of graphite will permit it to be invaded by the coolant to the extent of perhaps another 10 per cent of its volume, a satisfactory breeding gain appears possible only with bismuth or lead, particularly the former.

In Table 5 the neutron losses (per fission) to the coolant and to the graphite are given for various coolants and for various values of r, the moderating ratio N_c/N_{23}. In all cases a solidity of 0.9 is assumed, i.e., one-tenth of the core volume is occupied by coolant passages.

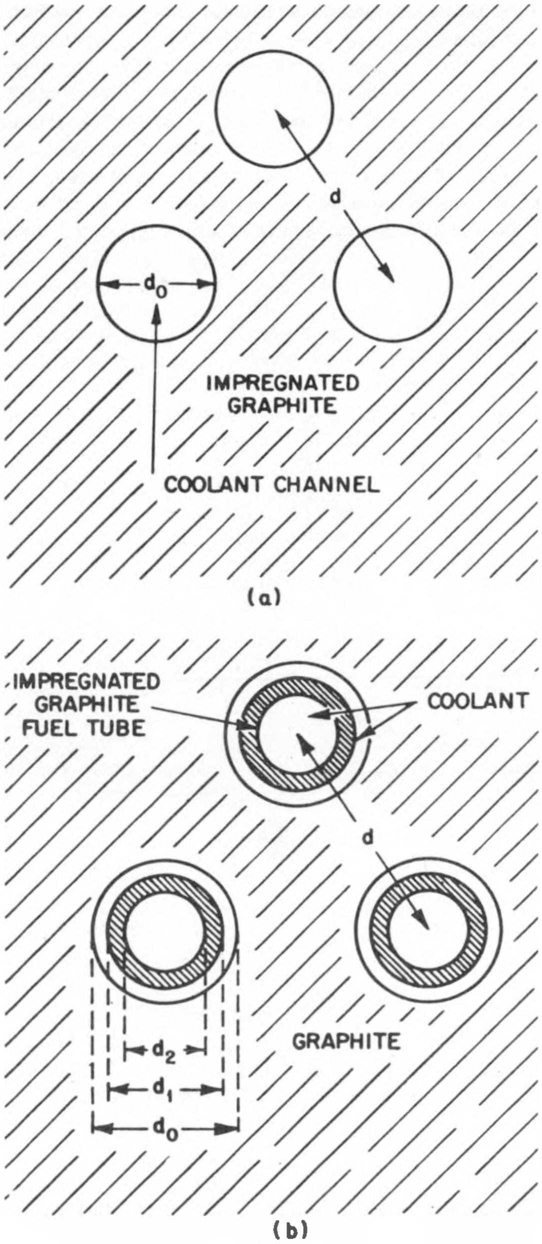


Fig. 6—Two versions of coolant channel layout. (a) graphite core homogeneously impregnated with fuel. (b) only tube impregnated with fuel.

Since $\eta - 2 = 0.35$ for U^{233} and since there will be other losses due to chemical processing, useless leakage, parasitic absorption in structure, etc., it is felt that only those cases in which the losses tabulated do not exceed 0.15 are of interest, and this implies that bismuth should be the choice for the coolant.

Table 4—Heat-transfer Performance for Cooling-channel Layouts of Figure 6
(Bismuth cooling; average power density in core, 750 watts/cm³; maximum stress in graphite, 2000 psi; height of core, h cm)

	S = 0.8		S = 0.9	
	Hole	Tube	Hole	Tube
d, cm	1.95	6.30	1.55	6.30
d_0, cm	0.89	3.63	0.49	2.56
d_1, cm		2.90		2.06
d_2, cm		1.80		1.27
Maximum temperature rise in graphite, ΔT_{max}, °C	347	400	332	398
Average power in fuel element, watts/cm³	938	5,560	833	11,060
Coolant speed, cm/sec	4.56h	4.56h	9.12h	9.12h

For this reason further calculations on reactor critical mass, neutron economy, and, in fact, those on heat transfer leading to the data of Table 4 were restricted to the use of bismuth as the coolant. Calculations were made on one of the typical examples, a homogeneously impregnated right circular cylinder of solidity 0.9. Two cases were considered: (a) the case in which the coolant resides only in the coolant passages and (b) the case in which the coolant invades the graphite. In each case nuclear constants and densities appropriate to 1500°C were used; the core was considered bare and no account was taken of possible reflector savings. The results for case (a) are given in Table 6. The total reactor power W is computed assuming a power density of 750 watts/cm³, which appears to be a readily attainable value. The column labeled t_B is the time in days required to achieve 15 per cent burn-up of fuel, assumed as before to be about the maximum permissible. The quantities t_{d0}, t_{d4}, and t_{d8} next tabulated are the doubling times when (1) no fuel other than that present in the core is invested, (2) the chemical-processing cycle for a core takes four days, and (3) the chemical cycle takes eight days, respectively.

Evidently a minimum doubling time for this system in the range of 200 to 300 days can be achieved, depending on permissible burn-up, neutron economy, and chemical-processing cycle time. Going to a solidity of 0.8 does not significantly affect the critical mass, and it raises the neutron losses only slightly. Therefore, heat transfer will not be a serious limitation to specific power in a reactor of this type. The critical mass for the bare core is 27 kg, not unduly large; the total power is 2000 megawatts, which may be on the large side for a single unit of a power system.

714 154

DECLASSIFIED

Similar results are given for case (b) in Table 7. Experiments to date have indicated that the graphite pore volume is partially filled with liquid metal, so this may be a more realistic case. It is at first surprising to observe that the critical mass is smaller for a given value of r in the case where the graphite pores are filled with coolant. This arises from the fact that the macroscopic absorption cross section of bismuth is nearly the same as that of graphite, while the macroscopic scattering cross section is considerably higher when the graphite voids are filled. The decrease in thermal utilization due to the presence of additional bismuth in the pores is more than compensated for by the decrease in migration length in the graphite-bismuth mixture, which is a consequence of the strong scattering by bismuth, even though it has no slowing-down power by itself. However, while the critical mass is significantly reduced, the breeding gain is decreased by the presence of additional bismuth, and the over-all effect on the doubling time is to raise it slightly.

Table 5—Neutron Losses Per Fission to Graphite and Coolant vs. $r = N_c/N_{23}$
[Core solidity S = 0.9; (a) coolant in cooling channels only; (b) coolant in both coolant channels and voids in graphite]

Values of r	20,000	10,000	8,000	5,000	3,000	2,000	1,000	500
Coolant:								
Bi (a)	0.22	0.11	0.09	0.05	0.03	0.02	0.01	
(b)	0.32	0.17	0.13	0.08	0.05	0.03	0.01	
Sn (a)	1.46	0.73	0.58	0.37	0.22	0.15	0.07	0.04
(b)	4.60	2.30	1.90	1.20	0.70	0.47	0.15	0.08
Pb (a)	0.60	0.30	0.24	0.15	0.09	0.06	0.03	0.02
(b)	1.70	0.84	0.67	0.42	0.25	0.17	0.08	0.04

A minimum value in the same range, 200 to 300 days, can still be attained in a system where the critical mass is about 20 kg and the total power is about 1400 megawatts. It thus appears that, so far as fuel inventory, doubling time, and total power are concerned, invasion of the graphite by the liquid metal coolant is an advantage. In addition, this phenomenon may serve to mitigate the probable reduction in thermal conductivity of graphite by radiation during the operation of the core. A disadvantage, however, may be the possible reduction in the rate of diffusion out of the core of the fission-product poisons. Experimental work on these points is required, but it appears evident that this phenomenon is not a major obstacle to the use of impregnated graphite directly in contact with a liquid metal coolant.

Preparation and Chemical Stability of Impregnated Graphite Core

The core is envisaged as a cylinder 1 to 2 meters in height and diameter, perforated axially by channels through which the coolant is pumped. The graphite is impregnated with U^{233} as UC_2. The fertile material is thorium and may be located either in the core or in a surrounding breeding blanket, more probably in the latter. The thorium could be impregnated in the blanket graphite, which is required to thermalize the fast-neutron leakage from the core, could be present there in a fluidized form[6] as a $Th(OD)_4$ slurry in D_2O, or it could be used as ThF_4 pellets in a graphite matrix. The last-mentioned scheme has been studied extensively at Brookhaven National Laboratories[7] and appears to be the best of the possibilities considered so far.

The uranium density required, of the order 10 mg/cm^3, can be attained by existing practice, as described in detail in Report NAA-SR-36.[8] In outline, the procedure is to evacuate a vessel containing the core and then introduce an aqueous solution of uranyl hexahydrate (UNH). The subsequent steps are

1. Pressurize solution with 150 psi air.
2. Drain excess solution, after sufficient time for diffusion into the graphite.
3. Introduce NH_3 at 120 psi, and raise graphite temperature to about 150°C.
4. After sufficient time for NH_3 diffusion, pump out vessel and heat gradually to about 300°C.
5. In an atmosphere that is inert, continue heating to 2500°C.

The reactions involved are (schematically)

$$UO_2(NO_3)_2 \xrightarrow{NH_3} (NH_4)_2U_2O_7 \xrightarrow{300°C} UO_3 \xrightarrow{2500°C} UC_2$$

The use of ammonia provides a more uniform dis-

Table 6 — Reactor Performance vs. Moderating Ratio r = N_c/N_{23}

(Bismuth cooling; core solidity S, 0.9; average power density in core, 750 watts/cm³; neutron losses (l_0) in chemical processing, useless leakage, parasitic absorption, etc., 0.15; coolant in cooling channels only)

r	Neutron losses in core (l_c)	Total neutron losses ($L = l_c + l_0$)	Critical mass (M_c), kg	Volume of core (V), cm³	Total power (W = 750V), megawatts	Specific power in core ($W_r = W/M_c$), megawatts/kg	Time for 15% burn-up (t_B), days	Doubling time (t_{d0}) for zero chemical-processing time, days	Doubling time $\left(t_{d4}\ \frac{4 + t_B}{t_B}\ t_{d0}\right)$ for four days chemical-processing time, days	Doubling time $\left(t_{d8} = \frac{8 + t_B}{t_B}\ t_{d0}\right)$ for eight days chemical-processing time, days
20,000	0.22	0.37	19.0	1.3×10^7	9,700	510	0.27	∞	∞	∞
10,000	0.11	0.26	18.0	6.0×10^6	4,500	250	0.54	28	235	440
8,000	0.09	0.24	19.0	4.8×10^6	3,600	190	0.71	30	200	370
5,000	0.05	0.20	24.0	3.5×10^6	2,600	108	1.30	39	160	280
3,000	0.03	0.18	27.0	2.7×10^6	2,000	74	1.80	50	160	270
2,000	0.02	0.17	33.5	2.3×10^6	1,700	51	2.70	69	172	275
1,000	0.01	0.16	52.0	1.8×10^6	1,350	26	5.20	128	226	325

Table 7 — Reactor Performance vs. Moderating Ratio r = N_c/N_{23}

(Bismuth cooling; core solidity S, 0.9; average power density in core, 750 watts/cm³; neutron losses l_0, 0.15; coolant both in cooling channels and in pores of graphite)

r	Neutron losses in core (l_c)	Total neutron losses (L)	Critical mass (M_c), kg	Volume of core (V), cm³	Total power (W = 750V), megawatts	Specific power in core ($W_r = W/M_c$), megawatts/kg	Time for 15% burn-up (t_B), days	Doubling time (t_{d0}) for zero chemical-processing time, days	Doubling time $\left(t_{d4} = \frac{4 + t_B}{t_B}\ t_{d0}\right)$ for four days chemical-processing time, days	Doubling time $\left(t_{d8} = \frac{8 + t_B}{t_B}\ t_{d0}\right)$ for eight days chemical-processing time, days
20,000	0.34	0.49	14.0	9.8×10^6	7,400	530	0.25	∞	∞	∞
10,000	0.17	0.32	13.0	4.3×10^6	3,200	250	0.54	84	700	1,330
8,000	0.14	0.29	13.6	3.5×10^6	2,600	190	0.71	55	365	675
5,000	0.09	0.24	15.9	2.5×10^6	1,900	120	1.1	48	220	395
3,000	0.05	0.20	19.4	1.9×10^6	1,400	72	1.9	58	180	300
2,000	0.03	0.18	24.0	1.65×10^6	1,200	50	2.7	74	185	292
1,000	0.01	0.16	36.0	1.4×10^6	1,000	28	4.8	120	220	320

tribution of uranium in the graphite than is obtained by direct drying and heating of the nitrate-impregnated material. If such uniformity is not necessary, the ammonia step may be omitted.

Core Stability

1. Reaction with Coolants. If helium gas cooling is used, erosion is the most likely damaging process that could occur. However, experiments discussed[9] in Report NAA-SR-77 show that there is no erosion of graphite surfaces at 2000°C by helium gas moving at velocities up to Mach 0.5. These experiments were made in the absence of radiation.

Table 8 — Behavior of Several Liquid Metals in Contact with Graphite

Liquid metal	Melting point, °C	Boiling point, °C	Test temperature, °C	Time, hr	Observed behavior	Stable carbide
Sn	232	2730	1800	24.0	No attack	None
Pb	328	1740	1260	7.0	No attack	None
Mg	650	1125	800	7.0	No attack	None
Bi	271	1630	1130	7.0	No attack	None
Al	659	2330	1580	7.0	Attacked badly	Al_4C_3
				3.5	Attacked badly	
				0.2	Attacked badly	
Na	97	904	900	24.0	Unsatisfactory	Na_2C

Core stability toward possible liquid metal coolants at temperatures up to 2000°C cannot be accurately evaluated on the basis of available data. However, a series of preliminary measurements on the behavior of a number of liquid metals in contact with graphite has been carried out with the results[10] to date given in Table 8.

These data indicate that Sn, Pb, Mg, and Bi should perform satisfactorily as coolants.

There is little probability that the uranium would be removed from the core by any of the materials listed in Table 8, because of the stability of UC_2.

There are no data on the effect of radiation on corrosion in the systems considered here. Although radiation is known[11] to retard the corrosion of aluminum by water, serious consideration must be given to the possibility that the intense radiation in the reactor core may adversely affect the corrosion facts indicated in Table 8.

2. Diffusion of UC_2 Fuel. Under the contemplated conditions of operation, diffusion of the fuel from the core into the surrounding structures or into the coolant stream is not significant. This conclusion is based on experiments, carried out in the absence of radiation, described in Report NAA-SR-64.[12] In these experiments a graphite sleeve was pressed over a cylindrical impregnated graphite core, and the assembly was heated at temperatures up to 2500°C. From the observed diffusion rates it is calculated that after 1000 hr at 2000°C the uranium content in the sleeve is less than 1 per cent of the core concentration in the first millimeter adjacent to the core and 10^{-4} per cent in the second millimeter from the core. These results show that negligible diffusion of UC_2 will take place.

Core Operation

1. Radioactivity Produced. Table 9 summarizes the radioactivity of the core as a function of cooling time, following operation for two days at 1500 megawatts and assuming that no fission products leave the core. The activity at zero cooling time is about 90 per cent of the saturation activity. Calculations were based on Report NAA-SR-45.[13]

2. Diffusion of Fission Fragments from the Core. Experimental results given in Report NAA-SR-72[14] show that fission fragments will diffuse out of graphite when heated to a high temperature in vacuum. Typical results are that (1) practically all the Ba^{140} and Sr^{89} activities diffuse out of graphite within 5 min at 2000°C and within 30 min at 1880°C and that (2) more than 95 per cent of the Zr^{95} activity remains in the graphite even after 5 hr at 2000°C. These observations were made, in the absence of radiation, on uranium oxide–impregnated graphite specimens ⅜ in. in diameter by

$\frac{1}{8}$ in. thick, at times of about one to three months after removal from a reactor.

The above experimental conditions differ in several respects from the situation in the proposed reactor core: (1) The samples were allowed to come into contact with air before the diffusion anneal, therefore, oxidation of the fission products could have occurred; (2) the graphite was impregnated with UO_2 instead of UC_2; (3) considerable time elapsed between the irradiation and the subsequent diffusion anneals; and (4) no radiation was present during the high-temperature diffusion. The fact that diffusion from the core can occur instantaneously in the reactor following fission favors more complete elimination of the fission fragments from the core. This is so because of the high percentage of volatile elements which are first members of decay chains, e.g., Se, Br, Kr, Rb, Sb, Te, I, Sr, and Xe. High ambient coolant pressure in the core would retard the diffusion rate, but the actual comparison with vacuum conditions would depend on the configuration of the core (thickness of graphite between coolant ducts), the permeability of the graphite, and other variables. Finally, the radiation present in the core may increase the diffusion rate.[15]

Table 9—Core Activity as a Function of Cooling Time
(All fission fragments retained)

Cooling time	Activity, curies
0	8.0×10^9
1 hr	1.9×10^9
1 day	2.8×10^8
1 week	2.4×10^7
2 weeks	2.3×10^7

If it is assumed that all the fission fragments except those which form nonvolatile carbides will diffuse out of the core at 2000°C, the conclusion summarized in Table 10 is reached regarding those elements which remain.

The activity remaining in the core, as a function of cooling time, is shown in Table 11 for the most favorable case, namely, that only Zr, Cb, Mo, Y, and Tc remain in the core. In the calculation (based on reference 13), it was assumed that all krypton isotopes with half lives shorter than 3 sec will not substantially diffuse away before decay occurs.

3. Distribution of Activity in the Reactor System. The fission-product activity remaining in the core, and having diffused out of the core, after 15 per cent burn-up and after various cooling times following operation is listed in Table 11. The volatile fission products will be released into the coolant at the operating temperatures contemplated. With helium as the coolant these will be removed by condensing on cold surfaces in the portion of the system following the reactor, and with bismuth as the coolant the gaseous products can be removed by a suitable degassing process, the others by side-stream oxidation and scavenging of the oxides or by a salt-contacting method as developed at Brookhaven National Laboratory.[16]

Chemistry of Core Processing

A major limitation on the doubling time for the breeding cycle arises from the chemical-processing complex. The power breeder system is only of interest if it operates in a continuous fashion, and the flow of fuel through the reactor, separating plant, and core refabrication plant must be designed to keep the total inventory of fissionable material in the system at a minimum. Following operation of the reactor core up to the 15 per cent burn-up contemplated, it would be removed either as a unit or in part, depending on how uniform the burn-up is over the core, and started through the reprocessing plant. As soon as the spent core is removed, it is replaced with a reprocessed core which has just been received from the chemistry plant. To reduce the down time of the system, a branched coolant flow system and a parallel arrangement of two reactors would probably be used, so that, when one goes off the line for reprocessing, the second is immediately brought into operation. Meanwhile, the spent core is sent through the decontaminating, fuel recovery, and reimpregnating cycle.

Table 10—Elements Remaining in Core at 2000°C

Most probable	Less probable	Least probable
Zr	Ru	Ce
Cb	Rh	Pr
Mo		Nd
Y		Pm
Tc		Sm
		Eu

1. Decontamination by Diffusion and by Cooling. During operation the core will lose some fission-product activity by diffusion, even though the optimum "activity diffused from core" indicated in Table 11 will probably not be achieved. Despite the large absolute value of the activity diffused away, however, Table 11 shows that even in a favorable case, diffusion provides a decontamination factor no greater than 14. It therefore does not appear worth while to include a vacuum-bake step in the uranium recovery procedure. Table 11 indicates that there is little advantage in cooling times greater than about two days.

DECLASSIFIED

2. Chemical Recovery and Decontamination of Uranium. A two-step process is required to recover the unburned uranium in sufficient purity for reimpregnation in another core. The core is first leached to remove the uranium, and the uranium is then put through any of the accepted procedures[17] for decontamination and purification.

Experiments with electrolytic leaching of impregnated graphite, performed at NAA,[14] have indicated a 99.8 per cent recovery of uranium. The graphite is immersed in dilute nitric acid; it is made anode toward a platinum electrode; and a voltage of about 10 volts direct current is applied.

The adaptation of one of the well-established recovery processes to uranium involves no insurmountable obstacles other than high dilution. Since reactor operation at elevated temperature will provide some decontamination by diffusion, the uranium recovery process will not have to bear the full burden of decontaminating some of the fission products. Table 10 indicates that Zr, Cb, Mo, Y, Ru, Rh, and Tc tend to concentrate in the core, especially at 2000°C reactor operation. It will therefore be necessary to modify decontamination procedures for these elements. For example, it was found[18] that zirconium and ruthenium are the elements which limit decontamination in some solvent extraction processes. Some special consideration may therefore be given to special scavenging agents for these elements. This type of approach should be brought to bear on the final selection of the recovery process.

An additional factor in regard to processing the core is that the levels of activity per unit weight of uranium are far higher than usually encountered. This may involve problems in the radiation decomposition of chemical-processing materials, as well as unusual heat-generation problems from the intense radioactivity. The core has a critical mass of about 20 kg, and consequently after 15 per cent burn-up it contains about 3 kg of fission products. After two days of cooling subsequent to a two-day operating period, the radioactive power from these fission products is about 400 watts/g. The fission-product activity per gram of uranium is greater in the reactor core considered here than in the case of the uranium being chemically processed at Hanford. Experiments early in the Manhattan Project indicated that a level of activity several hundred times higher than those prevailing in Hanford processes can be tolerated. The use of greater dilution may, therefore, be all that is required to circumvent difficulties in chemical reprocessing from the very high specific activity of this core.

An experimental program on this problem is now being undertaken, with particular emphasis on the possibilities of the BrF_3 fluoride volatility process. Since the uranium is in a graphite matrix, the direct application of BrF_3 to the core may generate large amounts of CF_4 rapidly. A method for obviating this difficulty must be devised. Once this obstacle is overcome, there is encouraging evidence that the fluoride separation of uranium from fission products can be utilized.

The important bearing of the chemical-processing system on the performance of the reactor complex has been very well described in a previous article in this journal.[19]

In general, the uranium recovery attainable from decontamination processes[14] is at least 99 per cent, at decontamination factors of 10^5. The latter factor implies that about 1 part in 100,000 of the fission-product elements would be left with the uranyl nitrate to be used for reimpregnation of a new core. (Maximum activity remaining with the uranium after a single processing would be about 4×10^4 curies.)

The time required for completion of chemical processing cannot be accurately estimated. In general, the fact that the desired end product is uranyl nitrate solution will contribute to keeping the time at a minimum.

Table 11 — Distribution of Activities after Diffusion at 2000°C

Cooling time	Core activity* (zero diffusion), curies	Residual core activity (favorable diffusion), curies	Activity diffused from core (favorable diffusion), curies
0	8.0×10^9	3.8×10^9	4.2×10^9
1 hr	1.9×10^9	2.7×10^8	1.6×10^9
1 day	2.8×10^8	4.2×10^7	2.4×10^8
1 week	2.4×10^7	5.5×10^6	3.8×10^7
2 weeks	2.3×10^7	1.7×10^6	4.0×10^7

*See Table 9.

DECLASSIFIED

3. Estimated Cycle Time. The largest uncertainty lies in the uranium reprocessing time. Nevertheless, a cycle time of eight days (from the time the core leaves the reactor to the reimpregnation of the recovered uranium into another core) appears possible according to the following estimate: removal and cooling, two days; leaching and filtering, one day; solution processing, three days; and reimpregnating, etc., two days. The procedures involved in the sequence of chemical operations, once the uranium is removed from the core, bear many resemblances to those proposed for the homogeneous aqueous-solution reactor. The refabrication of the core is itself a chemical operation rather than a metallurgical operation as is the case for all other solid-core reactors hitherto proposed. Hence, the cooling time required for the decay of activity of uranium isotopes produced by higher order reactions and the degree of decontamination of the fuel are far smaller than is usually considered necessary. The impregnated graphite-core reactor makes possible high specific power per over-all inventory of fuel because of the possibility of rapid chemical processing and refabrication, and, in addition, since it operates at high temperature, makes the production of excess power possible.

The proposed reactor and chemical-processing cycle are depicted schematically in Fig. 7. The power plant for the system is discussed in the following section.

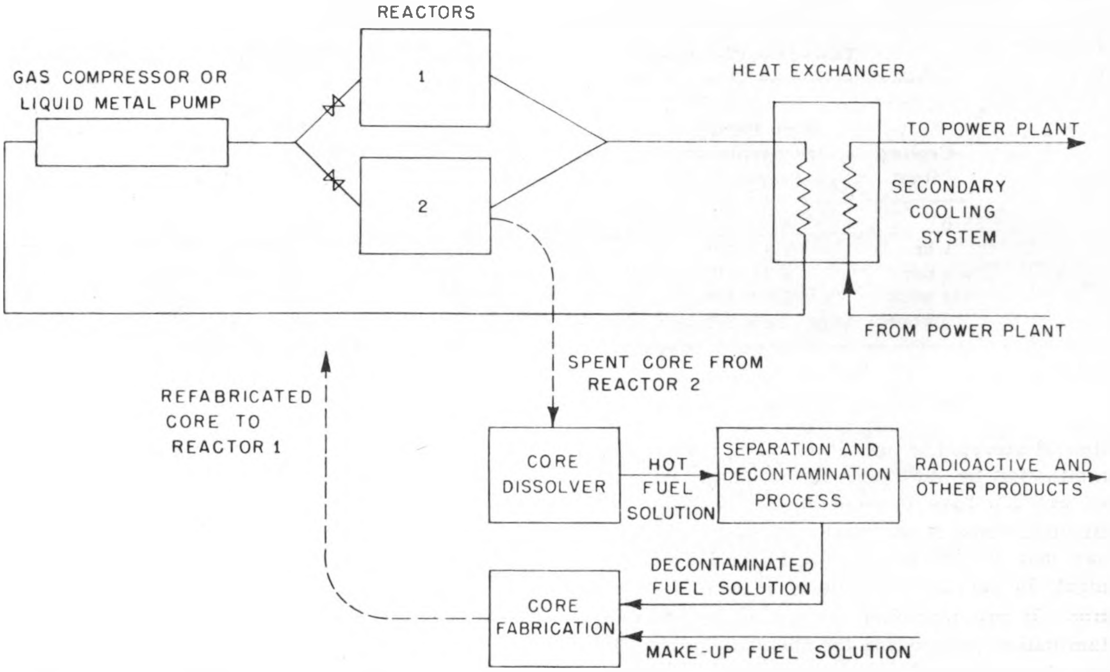


Fig. 7—Schematic diagram of proposed reactor and chemical process cycle.

EXTERNAL POWER SYSTEM

The problems of obtaining useful external power have been considered in Report NAA-SR-63,[1] where it was concluded that the gaseous power plant utilizing heat from a source below about 2000°C could not compete for efficiency with the presently available steam or mercury liquid-vapor power systems. Consideration of gaseous power systems is hence warranted only where, because of extreme local conditions, a liquid-vapor medium cannot be made readily available.

Whether or not a power plant using a liquid-vapor power medium can produce power in excess of the cooling requirements of the reactor is a function of the top temperature available to the liquid-vapor power system and of the pumping power required by the reactor. For a liquid metal—cooled reactor the pumping power required is low (about 1 per cent of the total reactor power for conditions discussed here). Since temperature drops in heat exchangers also can be made extremely low for liquid metal systems, the top temperature available to the power plant is little below that of the liquid metal-cooled reactor; therefore, the efficiency, and hence the external power output of the liquid metal—cooled reactor and liquid-vapor power plant system, is limited only by the temperature of operation of the reactor. Temperatures within the limits of present power plant practice would probably

DECLASSIFIED

give over-all plant thermal efficiencies of around 30 per cent.

The gas-cooled reactor requires both relatively large temperature drops across heat exchangers and relatively large pumping power requirements (of the order of 20 per cent for the conditions discussed here). Although it may be possible to design power plants operating with the source temperature provided by the gaseous heat exchanger which will provide an excess over this 20 per cent power requirement, it is probably necessary at the present stage of development to consider the power plant based on a gas-cooled reactor as a null-work system and to justify it on its breeding potentialities alone.

If the supply of fissionable material is limited, even including breeding possibilities, and if, as the present emphasis on design of power reactors indicates, a useful power output from the consumption of fissionable material is desirable, then it is expedient to evaluate the dependence of the efficiency of power production on various criteria. As is well known, a critical measure of the thermodynamic efficiency of a power cycle is the ratio of the top temperature of the cycle to the temperature of the ambient atmosphere. In order to achieve a high temperature-ratio cycle, it is necessary to have both a source of thermal energy at high temperature (reactor) and a high-temperature prime mover (turbine). In general, the top temperatures used in power plants are limited only by the capabilities of available materials for withstanding these temperatures.

Analytical studies[1] of the thermodynamic characteristics of power plant cycles have been made to determine the over-all thermodynamic efficiency and power output as functions of component efficiency and cycle temperatures. A typical result of this analysis is shown in Fig. 8 as applied to a simple open-cycle gas turbine having the component efficiencies: compressor, 80 per cent; turbine, 85 per cent; and combustor, 95 per cent. For comparison, the Carnot efficiency and the efficiency of an idealized liquid-vapor cycle are shown, as well as the efficiency for a gas turbine cycle having 100 per cent component efficiency. From Fig. 8 it can be seen that the benefits to be gained from an increase in the temperature ratio are many, particularly for a power cycle which is initially operating at low efficiency. For a cycle which is already in a region of high efficiency, the increases in efficiency for further increases in temperature are less, although the power output continues to increase at a rapid rate.

From the curves of Fig. 8 it can also be seen that there is a region of vanishing returns of efficiency as the temperature is continuously increased. It becomes necessary, therefore, to balance the benefits to be gained from high-temperature operation against the developmental limitations on structural materials and working fluids at these temperatures.

For the gas-turbine cycle shown in Fig. 8, increasing the temperature ratio from 3 (about present practice for gas turbines) to 6 would approximately multiply the thermodynamic efficiency of the cycle by a factor of 3.5 and multiply the power output per pound of working medium by about 7.5. In a power plant designed to give a certain power output, the over-all effect of this temperature change would be to decrease the fuel consumption to about one-third of its original value and to decrease the power plant size and weight by an amount dependent on design configuration. It can be seen then that, if nuclear materials are economic items, or if fuel reprocessing is expensive, the top temperature of the cycle must be maintained as high as possible.

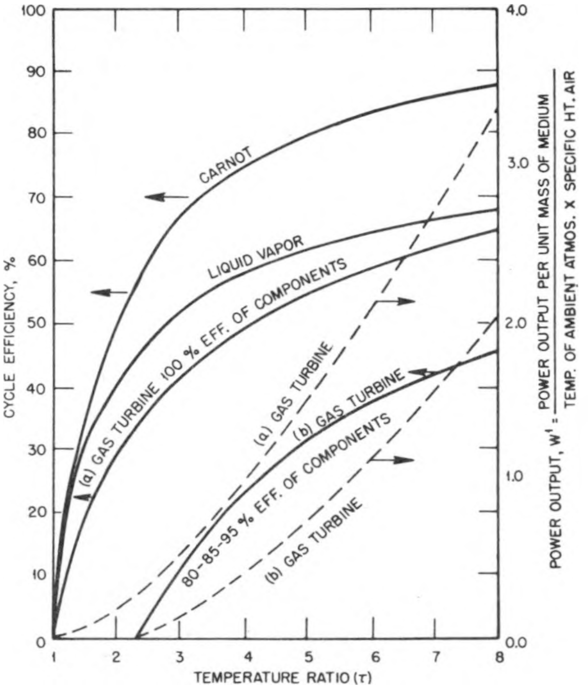


Fig. 8—Power plant performance. —, cycle efficiency. – – –, power output.

The scope of the materials problem is such as to preclude detailed discussion in this article. Briefly, results of considerable experimental work on graphite show that this material has attractive tensile strength and creep properties at high temperature. On a strength-to-weight ratio basis, certain types of graphite at temperatures of the order of 2000°C compare favorably with the best gas-turbine alloys op-

714 161

erating in their applied temperature range of approximately 1060°C. In addition to graphite, the properties of molybdenum, tungsten, and tantalum suggest possible applications in various components of the high-temperature cycle.

SUMMARY AND CONCLUSIONS

A high-temperature reactor based on the use of graphite impregnated with enriched uranium appears to offer improved characteristics for power breeder application.

Table 12—Reactor-system Performance Characteristics

	Coolant			
Characteristics	Helium		Liquid bismuth	
Reactor power, megawatts	1500		1400	
Critical mass, kg	20		20	
Burn-up, %	15		15	
Reactor operating time, days	2		1.9	
Chemical reprocessing time, days	4	8	4	8
Reactor specific power, megawatts/kg	67	67	72	72
Cycle specific power, megawatts/kg	22	13.5	23	13.8
Doubling time, days	280	450	180	300
Pumping power, megawatts	450		10	
External power:				
33% plant efficiency, megawatts	0		470	
50% plant efficiency, megawatts	200		700	

A liquid-bismuth-cooled reactor, in which U^{233} is bred from thorium, operating in the region near 1500°C appears to present no insurmountable obstacles, although a large number of development problems remain to be investigated and solved. These include

1. Methods of fabricating the reactor system from graphite alone or from other suitable refractory materials
2. The effect of radiation on the thermal conductivity of graphite at elevated temperatures
3. The design of a pumping system and heat exchanger operating with liquid metal near 1500°C
4. The development of a core-reprocessing chemical cycle which can handle spent fuel rapidly in the face of extremely high specific activity
5. The development of a continuous-flow breeding-blanket chemical cycle

If these problems can be adequately solved, it appears that the achievement of a thorium-U^{233} power breeder system with the characteristics shown in Table 12 is feasible.

ACKNOWLEDGMENTS

This paper is based on work which has been carried on for the past several years by a large group of scientists and engineers in the Atomic Energy Research Department of North American Aviation, Inc. Much of the material was prepared for the author by the men carrying on investigations in each relevant field. The experimental information on properties of graphite has been obtained by C. Malmstrom and R. L. Loftness. The heat-transfer calculations are the work of T. Omori (helium) and M. Heisler (liquid metals). The section on power plant costs is based on studies by R. Elliott and J. Malone. The section on chemical processing is based on material furnished by H. Pearlman and E. Motta; that on the external power system is based on studies by S. Thompson.

Throughout the preparation of the paper the author has benefited from discussions with C. Malmstrom, R. Stoker, and C. Starr.

REFERENCES

1. W. C. Parrish and H. Schwartz, High Temperature Power Cycles, Report NAA-SR-63, July 1950.
3. M. C. Udy and F. W. Boulger, The Properties of Graphite, Report BMI-T-35, June 1950; C. Malmstrom et al., J. Applied Phys., 22: 593 (1951).
4. L. P. Hunter, J. Met. Ceram., 2: 41 (January 1949) (discussion of original experiments). Later experiments not in good agreement with these are given by R. G. Berggren et al., Report ORNL-576, Feb. 7, 1950, p. 12.
5. R. W. Dayton et al., A High Power Density Gas-cooled Reactor-core Configuration, Report BMI-T-27, May 1950; see also R. W. Dayton, Battelle Memorial Institute, RAND Report R-111, Aug. 10, 1948.
6. S. S. Kistler et al., Ind. Eng. Chem., 26: 388 (1934); H. B. Weiser, "Inorganic Colloid Chemistry," Vol. II, p. 271, John Wiley & Sons, Inc., New York.
7. Progress Reports of Reactor Science and Engineering Department, Brookhaven National Laboratory, Reports BNL-48, BNL-52, BNL-67, BNL-88, and BNL-95 (sections on continuous-separation breeding blanket by F. T. Miles).
8. G. N. Steele, Studies on the Impregnation of Graphite with Uranium, Report NAA-SR-36, June 1950.
9. L. Green, The Erosion of Graphite by High Temperature Helium Jets, Report NAA-SR-77, May 1950.
10. C. R. Malmstrom and R. L. Loftness, North American Avaition, Inc., unpublished data.
11. O. A. Allen et al., The Effect of Radiation on the Corrosion of Metals by Water, Report CC-1677, July 6, 1944.
12. R. L. Loftness, Diffusion of Uranium Carbide in Graphite, Report NAA-SR-64, August 1950.

162

DECLASSIFIED

13. J. K. Thornton and W. Houghton, The Activity of U^{235} Fission Products, Report NAA-SR-45, September 1950.
14. C. A. Smith and C. T. Young, Diffusion of Fission Fragments from Uranium-impregnated Graphite, Report NAA-SR-72, May 4, 1951.
15. G. J. Dienes and M. H. Feldman, An Experiment Proposed for the NAA Statitron. Silver Self-diffusion in a Radiation Field, Report NAA-SR-Memo-22, Mar. 15, 1951.
16. D. H. Gurinsky et al., Tentative Design for a Uranium-Bismuth Liquid-fuel Power Reactor, Report BNL-105, p. 9, Apr. 27, 1951.
17. Tabulation of Metal Recovery Processes, Report TID-251, Mar. 8, 1949.
18. W. B. Lanham and A. T. Gresky, Purex Process Laboratory Development, Report ORNL-717, June 1950, p. 25.
19. M. Benedict et al., Reactor Sci. Technol., 1: 96 (1951).

June 1951

DECLASSIFIED

[redacted]

PROBLEMS OF RADIATION DAMAGE IN LIQUIDS

By A. O. Allen

Brookhaven National Laboratory

Report BNL-1012 (Del.)

ABSTRACT

Current research is surveyed on (1) basic studies of chemical-reaction mechanisms, rates of energy transfer, and modes of excitation of molecules by radiation; (2) materials testing and development, i.e., more or less empirical studies of the ways in which properties of materials are affected by radiation, development of materials more radiation resistant than those currently at hand, and development of practical uses for radiations; (3) reactor-component testing, which is essentially materials testing under the specific conditions which are to obtain at some particular point of a particular proposed reactor. Work on the effects of radiation on homogeneous reactor solutions, coolant or moderator water, and separation processes is reviewed briefly, and future investigations are recommended.

PURPOSE

This report surveys the state of knowledge and research in the field of radiation damage in liquids and related topics, with special reference to information which may be relevant to the design of nuclear reactors.

SCOPE

The main intent of this report is to consider effects occurring in the liquid phase. However, radiation effects on a substance depend not so much on the state of aggregation (solid, liquid, or gaseous) as on the nature of the bonds holding the atoms together, i.e., whether the bonds are covalent, ionic, or metallic. Most ordinary liquids are molecular covalent compounds. They consist of individual molecules, the atoms within the molecule being held firmly together by chemical valence forces, while the forces holding the molecules together are much weaker. Ordinary gases and liquids, such as air and water, are covalent compounds, as are the organic materials. Simple salts, on the other hand, are ionic compounds; their crystals consist of a group of electrically charged particles held together by electrostatic forces. Metals are held together by a third type of bond. In the case at least of molecular materials, observations show that radiation effects on a given substance in the vapor or solid state are similar to the results observed in the liquid state. Because of this similarity the whole field of radiation effects on covalent compounds has always been regarded as a unit, and the singling out of the liquid state for attention would be arbitrary. We therefore consider here the effects produced by radiation on molecular compounds, solid, liquid, or gaseous.

~~237 001~~

DECLASSIFIED

The phenomena produced by radiation in covalently bonded materials are caused essentially by the electronic excitation and ionization of the individual molecules composing the material. The principal phenomena are those which result from the breaking of the bonds within these molecules and the production of chemical changes.

In solid ionically bound materials, on the other hand, chemical changes are unimportant and the chief effects of radiation are to produce abnormal states of electrons in the materials, leading to coloration and changes in electrical properties. The study of radiation effects in such materials is essentially a separate field and will be hardly touched on here.

In metals, or semimetallic electrical conductors such as graphite, electronic excitation has little or no effect, and changes in such materials are brought about only by direct atomic collisions. These effects constitute still another field of study within the general topic of radiation damage, and researches in this field were surveyed exhaustively in the report of the Slater Committee, Report AEC-500. This report took the view that radiation effects on insulating materials or liquids were of minor importance for reactor construction and that major emphasis should be put on studies of effects of atomic collisions. With the present revival of interest in homogeneous reactors and further interest by reactor-design engineers in using covalent materials such as lubricants and plastics in radiation fields, the effects of radiation on liquids and insulators again assume some practical importance, and the state of knowledge in this field becomes of concern.

PROCESSES OCCURRING ON IRRADIATION OF MOLECULES

Literature Reviews

The field considered in this report is generally known by the name "radiation chemistry." Its primary concern is the study of chemical changes brought about by high-energy radiations. Many people are under the impression that very little is known about this field. Actually a considerable amount of literature exists on the subject, and probably as much is known about this subject as about many other fields of chemistry. No recent books exist which summarize the status of this field, but a number of good unclassified reviews have appeared in recent years. A general survey of the subject of radiation damage is given by the author in "The Science and Engineering of Nuclear Power," edited by Clark Goodman, Vol. II, Chap. 13 Addison-Wesley Press, Inc., Cambridge, Mass., 1949, also issued as Report MDDC-962. A review by M. Burton in "Annual Reviews of Physical Chemistry," Vol. I, pp. 113-132, Annual Reviews, Inc., Stanford, Calif., 1950, gives a somewhat more detailed discussion of the primary physical processes and presents more recently published material. Another good review with perhaps more emphasis on aqueous solutions is given by F. S. Dainton in "Annual Reports on the Progress of Chemistry," Chemical Society, London, Vol. 45, p. 5, 1948. All three of these reviews should certainly be read by anyone who wishes to become familiar with the field. This article will not attempt to cover the fundamentals of the subject as thoroughly as the above reviews, but it will give a brief statement of the nature of the physical processes occurring as an introduction to discussion of current research.

Absorption of Radiations

The radiations of particular importance to reactor design are the gamma rays, fast neutrons, and fission recoils which occur in all reactors. Gamma rays lose their energy in materials by the Compton effect, the photoelectric effect, and by pair production, all of which result in the production of energetic electrons which traverse the material. Fast neutrons lose energy by colliding with atoms of material and setting them in motion. The resulting fast atoms are ionized as a result of their high velocity and gradually lose energy as they move through the material. Fission recoils are rapidly moving, highly charged ions. Thus in all cases the actual transfer of energy to the molecules of the material is brought about by the passage of fast charged particles.

The loss of energy by charged particles passing through matter is a well-investigated subject, thoroughly discussed in books by Rasetti,[1] Pollard and Davidson,[2] and Rutherford, Chadwick, and Ellis.[3] Details of the processes are perhaps best understood for gases. Passage of a fast charged particle close to, or through, a

714 165

gas molecule perturbs the electronic system of the molecule, leaving the molecule in an electronically excited state and possessing excess energy. If the amount of energy transferred exceeds the ionization potential of the molecule, the molecule may emit an electron, thus becoming a positive ion. The emitted electron, if sufficiently energetic, may produce secondary ionization and excitation in its turn. If insufficient energy for ionization goes to the molecule, it is left in an electronically excited state, identical with the excited states formed in molecules by absorption of light. About equal amounts of energy are expended in most gases by ionization and by excitation. The probability of occurrence of the various excitation and ionization processes depends only on the velocity and electric charge of the moving particle, not on its mass. These probabilities increase rapidly as the moving charged particles slow down, so that the events occur much closer together at the end of a charged-particle track than they do at the beginning. Since a heavy particle, such as a proton or an alpha ray, moves much more slowly than an electron of equal energy, the range of electrons in matter is much greater than that of heavy particles of the same energy.

The rate at which charged particles lose energy in traversing matter depends almost solely on the number and kind of atoms present, irrespective of the state of combination of the atoms into molecules and of the state of aggregation, whether solid, liquid, or gaseous. However, the nature of the excited states formed in the material is known to be quite different in ionic solids than in gases. The condensation of a gas to form an ionically bound solid causes most of the excited states to degenerate and merge with the ionized state. A few of the lowest excited states may remain as such in the crystal (formation of "excitons") but the majority of excitation processes will send an electron into the conduction band, a state in which the electron is no longer bound to the atom but is free to wander through the material.[4] Most excitation processes thus become ionizations, and the energy required to produce the ionized state is only about one-half or one-third that required to produce an ionized gas molecule.

In liquids and molecular solids the nature of the excited states is not at all clear. Liquid compounds definitely appear to possess low-lying excited nonionized states similar to those of vapors, but we may expect that the excited states of higher energies are somewhat degenerate and that the distinction between excitation and ionization is less clear-cut in the liquid state than in the vapor state. Little or nothing is known about the higher excited states of any liquid. The amount of ionization produced by radiation, readily measured in gases, cannot be determined in ordinary liquids. Workers in radiation chemistry and radiobiology appear very prone to overlook the essential vagueness of the concept of ionization in the liquid state.

When a heavy charged particle approaches the end of its trajectory, it will pick up electrons from the surroundings and become a fast neutral atom. In this state it loses most of its remaining energy by "billiard-ball" collisions with other atoms.[5] Such collisions produce radiation effects but are important only in materials such as metals which are unaffected by excitation and ionization. In molecular materials the excitation processes are so much more important than the atomic collisions that the latter may be neglected.

Consequences of Excitation and Ionization

The energy of any electronically excited state of a molecule is practically always greater than the energy required to dissociate the molecule. Any excited molecule is likely to break up; such processes constitute the well-known reactions of photochemistry. Photochemical dissociations of this type certainly occur whenever molecular materials are subjected to ionizing radiation. In addition, the free ions produced in gases bring about chemical reactions in other ways. Positive ions have a great tendency to dissociate spontaneously.[6] They may also react with neighboring ordinary molecules to yield new types of ions, as in the well-known reaction of ionized hydrogen[7]

$$H_2^+ + H_2 \rightarrow H_3^+ + H$$

Ions may also transfer their charge bodily to neutral molecules of another kind.[8,21]

The electrons set free in the ionization processes may form negative ions, usually by adding to the electrophilic part of a molecule and dissociating it,[9,38]

DECLASSIFIED

$$e^- + H_2O = H + OH^-$$

The positive and negative ions eventually neutralize each other. The energy set free on neutralization is nearly equal to the ionization potential of the positive ion (usually over 10 ev),[10] which is sufficient to break two or more chemical bonds in the resulting molecules. Thus all sorts of dissociation processes are to be anticipated as a result of the ionization of molecules by radiation.

When a small molecule dissociates, the resulting products must practically always be free atoms or free radicals. Thus the dissociation of H_2O might occur in three ways,

$$H_2O \rightarrow H + H + O$$

$$H_2O \rightarrow H_2 + O$$

$$H_2O \rightarrow H + OH$$

The last process requires the least reorientation of chemical bonds and is thought to occur far more frequently than the other two.[11] With larger molecules, such as most organic compounds, dissociation into stable molecules is possible. Thus ethane might decompose directly to hydrogen and ethylene,

$$C_2H_6 \rightarrow C_2H_4 + H_2$$

The dissociation into free radicals would, however, be expected to occur more frequently,

$$C_2H_6 \rightarrow CH_3 + CH_3$$

$$C_2H_6 \rightarrow C_2H_5 + H$$

What is actually seen when materials are irradiated depends then on the subsequent behavior of the highly reactive free radicals formed in the dissociation process. An important part of radiation chemistry is, first, to explain observed reactions in terms of the free-radical reactions which brought them about and, second, to explain the way in which the particular free radicals are formed from the original molecules by the complex excitation and ionization processes described above. The nature of the free-radical reactions can be inferred by studying the reaction kinetics in particular cases and comparing results with free-radical reactions known from studies of photochemical or thermal reactions.

Although the ionization and excitation processes are thought to be the same for different kinds of radiation in any given material, the chemical effects of the different kinds of radiation are found to differ in detail.[12,58] The concentration of excited molecules or free radicals when they are formed in a charged-particle track is greater for slower moving particles, and this concentration affects the relative rates of the subsequent reactions. Thus radiation effects in any material are a function of the mean ionization density of the radiation; heavy-particle radiations may give different effects from electrons or gamma rays. The effect is especially prominent in water, which is decomposed to a much greater extent by alpha rays than by beta rays or X rays.

An important general problem underlying all such reaction mechanisms concerns the character of energy transfers which may occur between molecules, or from one part of a large molecule to another part, prior to the dissociation of the molecules.[13] If such transfers are rapid, we may expect a rather selective breakdown of weaker parts of the chemical system or perhaps a concentration of energy in those molecules or parts of molecules which are able to dissipate energy by emission of fluorescence rather than chemical dissociation. A good part of current research on radiation effects on organic compounds, or on macromolecules of biological interest, appears to be aimed at learning more about energy transfer in excited states.

Radiation Yields

The amount of chemical change occurring in a material under irradiation is usually expressed as the number of molecules reacting per unit energy input and is called the "yield." Complete study of a reaction would involve the determination of the yield as a function of temperature, pressure, concentrations, radiation intensity, and mean ionization density of the radiation. The unit usually employed for gases is the ion-pair yield M/N, defined as the number of molecules reacting per ionization produced. The preferred unit for liquids is the 100-ev yield G, defined as the number of molecules reacting per 100 ev of energy dissipated in the liquid. Some authors use a conventional ion-pair yield for liquids; this is the number of molecules reacting per 32.5 ev dissipated. Other units found are the micromoles per liter reacting per 1000 rep and the reciprocal yield, or number of electron volts dissipated per molecule reacting.

RADIATION SOURCES FOR RESEARCH

The study of radiation damage requires expensive sources of intense radiation. The study of reactions in solution generally requires doses of more than 10^5 rep, whereas the study of pure compounds may require more than 10^8 rep. Valuable auxiliary data can be obtained from such sources as electric discharges or ultraviolet lamps, but work with actual ionizing radiation is necessary. The available sources will now be discussed.

Reactors

Reactors are in many ways very poor research sources. The fast-neutron flux in a reactor, which is in most cases a chief source of radiation effects, varies rapidly from point to point within the reactor lattice and is generally not accurately known.[14,15] Moreover, the ratio of energy inputs by fast neutrons and by gammas may be an important factor in determining the amount and nature of chemical damage. This ratio is extremely variable among different reactors and is even less well known than the fast-neutron flux. The results obtained in one reactor therefore cannot be used to predict accurately the effects occurring in another reactor or even at another point in the same reactor. Most materials become highly radioactive when put into a reactor, and this greatly increases the experimental difficulties. Maintaining the irradiated specimen at a desired temperature is also usually more difficult with reactors than with other radiation sources. The radiation intensity on the specimen, as well as the nature of the radiation, can be varied only over rather narrow ranges, if at all. For these reasons it is better to use other radiation sources whenever possible.

Reactors have the advantage of delivering high-intensity radiation to larger volumes of material than can be accommodated by most other sources. They are useful in making qualitative or semiquantitative practical tests of the radiation resistance of materials or apparatus. The study of fast-neutron effects in solids (metals or graphite) requires the use of reactors. The main use of reactors in the field of radiation chemistry is to study processes triggered by thermal neutrons, especially the effects of fission recoils produced within a substance. Since the thermal-neutron flux at any point in a reactor is readily determined, many of the above objections do not apply in this case.

Cyclotrons

Cyclotrons are the most convenient source of heavy-particle radiation. The range of the cyclotron beam in materials is small, of the order of milligrams per square centimeter, and the area of the beam is generally only a few square centimeters, so that the amount of material that can be irradiated is always relatively small. This need not be a serious drawback if methods are available for the chemical analysis of small quantities, which is usually the case. Cooling of material need not be a serious problem if low beam currents are used. Radiation intensities can be varied over a wide range, and very large radiation doses can be obtained conveniently. Induced radioactivity in bombarded materials provides a handling difficulty, but this usually seems to be less serious than with reactor sources.

Van de Graaff Generators

Van de Graaff generators can be used either as sources of heavy particles or as sources of fast electrons or X rays. As heavy-particle sources they are less versatile than cyclotrons and have been used much less for radiation-effect studies. In studying the effects of electrons or X rays, however, they are unequaled.[16] Their output can be controlled very accurately over an extremely wide intensity range. Used as X-ray machines they provide the most intense source of hard X rays currently available. Used as cathode-ray sources which give radiation effects equivalent to those of hard X rays, they allow radiation intensity to be increased to practically any desired level.

X-ray Machines

X-ray machines exist in many types, most of which are adaptable to radiation-effects research. Their main limitation is in the intensity of radiation which can be obtained. They are less expensive than the machines described above, but their use is restricted to the study of systems in which measurable damage is produced by doses of less than about 10^5 rep.

Radioactive Cobalt

Radioactive cobalt is an excellent source of gamma radiation for chemical studies.[17,18] Sources of kilocurie strength are now available, giving intensities comparable to those of X rays from a Van de Graaff generator and higher than from most other X-ray machines. These sources require much less attention and maintenance than a machine, but they are not as suitable for problems requiring a wide variation in radiation intensities and cannot compete with cathode rays in the region of very high radiation intensities.

Natural Alpha Rays

Natural alpha rays provided the main radiation source for radiation chemical studies in the prewar days. Today the cyclotron supplies a controllable and versatile source of similar radiations. Multicurie polonium sources would provide a very handy high-intensity source of heavy-particle radiation for radiation-effect studies, and it would be very desirable if these sources could be made available to our laboratories.

Fission Products

Fission products produced in the large reactors are a potential source of gamma and beta rays of very high intensity, but the difficulties of preparing this material for such a use have hitherto resulted in a preference for radioactive cobalt sources.

Capacitrons

The capacitron[19,20] is a machine developed by A. Brasch and owned by the Electronized Chemical Corporation of Brooklyn. It has the unique property of delivering very large doses of 3-mev cathode rays, of the order of 10^8 rep, in pulses lasting only 1 μsec. The pulses are obtained by discharging, in series connection, a bank of condensers which had been charged up in parallel. The intensity during such a pulse is so great that one might expect instructively different chemical phenomena to occur with this machine as compared with ordinary sources. The machine is being promoted by its owner as a commercial device for the sterilization of foods and drugs, but its possible use as a research tool to study mechanisms of radiation damage should not be overlooked. No good basic studies of this sort have as yet been made with this machine.

Simulation of Reactor Radiation for Materials Testing

Designers of new high-flux reactors often fail to appreciate the fact that damage to covalently bonded materials proposed for use in their reactor can often be studied more effectively in a cyclotron beam or other simulated source than in a reactor. As appears from the above discussion, the effects of fast neutrons in a reactor, in so far as they result from ionization and excitation processes, will be identical to those produced from a beam of ions from a cyclotron having a velocity comparable to the speeds of the ions produced in the material by neutron impact. In a reactor we also find gamma rays, effects of which can be simulated completely by outside sources of gamma rays, X rays, or cathode rays. Such studies with simulated radiation are especially desirable when the proposed reactor is to operate at a higher flux than any available existing reactor. The cyclotron and Van de Graaff generator are capable of producing radiation intensities very much higher than those produced by the fast-neutron and gamma-ray flux of any proposed reactor. Moreover, as already remarked, such simulated radiation tests with machines are easier to carry out than tests in an actual reactor. Thus the data obtained with machines are equally meaningful and extend over a much wider range of radiation intensity, and also more extensive test data can be obtained in a given period of time.

Two kinds of radiation effects cannot be adequately simulated. One is the effect of fast neutrons produced through the agency of atomic collisions in materials like metals and graphite. These effects can be simulated to some extent by cyclotron beams, but the simulation is not nearly so adequate as in the case of covalently bonded materials where the damage is produced by ionization and excitation. The other agent which cannot be simulated is the fission recoil. These recoils are the most densely ionizing particles known, and study of their effects can be adequately made only by using actual fissions.

CURRENT RESEARCHES

Considered with respect to their aims, current researches in the field seem to fall in three categories: (1) basic studies of chemical-reaction mechanisms, rates of energy transfer, and modes of excitation of molecules by radiation; (2) materials testing and development — more or less empirical studies of the ways in which properties of materials are affected by radiation, development of materials more radiation resistant than those currently at hand, and development of practical uses for radiations; (3) reactor-component testing, which is essentially materials testing under the specific conditions which are to obtain at some particular point of a particular proposed reactor. These categories are obviously not very distinct, since materials testing always raises fundamental questions of mechanism and the reactor-component test always brings up questions of effects of changing conditions on the response of the materials. It is convenient, however, to separate our discussion of current researchers into these three categories.

Basic Studies

1. Gas-phase Reactions. The condition of molecules and the distribution of energy among them are certainly better understood from a physical standpoint in a gas phase than in a liquid phase. For this reason studies of reaction kinetics in the gas phase have always been thought of as more conducive to an understanding of basic processes than studies of liquid-phase reactions. In practice, reaction mechanisms in the gas phase have proved to be so complicated that a majority of researchers seem to prefer liquid-phase studies, in which reaction-rate correlations seem easier to obtain, although less detailed insight into the behavior of the molecules during the reaction is possible. The history of the study of the kinetics of thermal reactions shows that emphasis has gradually shifted from gas-reaction kinetics to solution kinetics, and a parallel tendency appears in the study of the kinetics of reactions brought about by high-energy radiations. Early work in this field, summarized in books by Lind[21] and Mund,[22] was largely concerned with the determination of products and yields in the reactions produced in gases by alpha rays. A large amount of valuable data was collected on the ion-pair yields of such reactions. Interpretation of all these data was originally made by the ion-cluster theory, but this proved unsatisfactory, and present-day thought on the subject follows lines indicated by Eyring, Hirschfelder, and Taylor.[23,24] These authors succeeded in interpreting ion-pair yields of some reactions of simple molecules by considering (1) the nature of the ions formed in the gas, as revealed by mass-spectrographic data, (2) the probable chemical reactions of these ions and of the excited molecules also formed by the radiation, and (3) the subsequent reactions of free atoms and radicals formed by dissociation processes. The kinetics of some simple reactions were explained in this way with some success, but the mechanisms were clearly so complex and the data on the nature of the ion and excited molecule reactions were so limited that a great deal of guesswork was required. In order to understand the processes thoroughly, the determination of ion-pair yields is clearly not enough. This fact seems to have deterred people in recent years from continuing to measure ion-pair yields in gaseous systems. At present, Mund[25,26] seems to be continuing such work on one or two reactions of hydrogen at the University of Louvain. Some work on UF_6 has also recently been carried out by Davis[27] at K-25, though the goal here was more to obtain information for engineering purposes than to gain insight into reaction mechanisms. To advance the study of reaction mechanisms, some attempt must be made to isolate the various kinds of processes occurring.

The initial processes of ionization can be studied in detail by determining the relative quantities of various ions formed in the mass spectrometer. A wealth of data is available here, and interpretation of the ionization process in terms of configurations and dynamics of the ionized molecules is being currently studied at an Atomic Energy Commission project at the University of Utah directed by Henry Eyring[28] and A. L. Wahrhaftig, at Brookhaven by Oliver Schaeffer,[29] and also in other laboratories.

Direct study of the subsequent behavior of these ions is a more difficult problem, to which a satisfactory approach has apparently not been found. Valuable clues are given in the study by Weisz[30,31] at the Socony Vacuum Oil Co., Inc., laboratories on the mechanism of discharges in Geiger counters. He has been able to determine the change in mobility of the positive ions with time after formation, which tells us something about the rates of the chemical reactions they are undergoing.

An instructive approach to the problem was initiated at Syracuse University in the 1930's by Essex,[32-36] who studied the effect of applied electric fields on the ion-pair yield of several alpha-ray–induced reactions. By this method some insight can be obtained into the fraction of the reaction which is initiated by excited molecules rather than by ions. Essex's project has progressed in understanding of the subject during the years, and he has recently shown that his method also yields information on the rate of production of negative ions in the gas by the electrons. The project is at present being continued under the direction of Benjamin Burtt. He expects to improve the experiments by the addition of an electron filter which will separate electrons from negative ions in the gas and allow more detailed measurements concerning the process involved in negative-ion formation.[37] This project seems to be the only current one in which fundamental mechanisms of gaseous radiation reactions are being studied experimentally. There is no question that more work of this sort is required to put discussions of reaction mechanisms in the liquid phase on a firmer basis.

A theoretical study of the processes of negative-ion formation has recently been published by Magee and Burton[38] of the University of Notre Dame. Theoretical work of this kind cannot progress very far without corresponding advances in experimental data, and it is fortunate that the experiments of Burtt appear to be proceeding in a direction to dovetail with the theoretical advances of Magee and Burton.

Studies of chemical reactions in a glow discharge have been published in great numbers in the past and Burton's AEC project at Notre Dame is currently engaged in studies on ammonia and hydrocarbons. The glow discharge is a convenient way of determining in a qualitative fashion what chemical products are to be expected under radiation, but quantitative interpretation of such work is very difficult.

2. Organic Compounds. A vast amount of old experimental data exists on the nature of reactions of organic compounds in electric discharges. This work is summarized in a book by Glockler and Lind.[39] Lind was able to show that the reaction products obtained by action of alpha rays on organic compounds are at least qualitatively similar to those obtained by electric discharge. We therefore know a great deal in a general way about what to expect when organic materials are irradiated. All organic compounds appear susceptible to chemical change by radiation; the products are never simple but consist of a mixture of compounds having molecular weights both lower and higher than the original material. Any hydrocarbon on prolonged irradiation turns into a complicated mixture resembling petroleum in its general characteristics. Formation of hydrogen gas is always a prominent feature, as is the production of materials of high molecular weight often called "polymers," although they appear not to have exactly the same elementary analysis as the starting material.

Much work has been done at Massachusetts Institute of Technology on the effects of alpha rays and cyclotron beams on fatty acids and a few similar materials by Whitehead, Goodman, Breger, and others under an American Petroleum Institute project on the origin of petroleum.[40-46] The object was to determine whether or not petroleum originated from the action of natural alpha rays in the ground on fatty sea-bottom deposits. The work did not succeed in making a very good case for this theory but did turn up some data of great interest in radiation chemistry. Detailed data were obtained on the reaction products from numerous fatty acids of various carbon-chain lengths. The decarboxylation reaction RCOOH → RH + CO_2 was found to be very prominent, even when the carbon chain R contained twenty or more carbon atoms, and good yields of the hydrocarbon RH were isolated.

714 171 ~~257 008~~

Thus, oleic acid yielded heptadecene, stearic acid gave heptadecane, etc. The bond combining the carboxyl group with the rest of the molecule was broken more frequently than any other bond in the molecule. This is a valuable indication that radiation can be a more specific reagent than was formerly thought, and it opens up possibilities for useful organic syntheses by irradiation. Yields of the various products were essentially the same whether the acid was bombarded in the solid state or the liquid state. A similar systematic study of the aliphatic alcohols under the cyclotron beam has recently been started by Amos Newton at the University of California Radiation Laboratory.[47] With the aid of such modern analytical techniques as mass spectrometry, much more complete material balances in these reactions have been obtained by the MIT group and by Newton than was possible in earlier investigations of electric-discharge reactions. Accumulation of such data will eventually lead to a better understanding of the reaction mechanisms and the relative importance of the various processes.

It has long been known that aromatic compounds are more resistant to radiation decomposition than are aliphatic compounds.[48] Burton, at Notre Dame, is particularly interested in studying reactions of benzene and other simple aromatics with a view to determining the nature of the energy-transfer processes which result in the aromatic stability. To this end studies have been made of the products formed in aromatic-aliphatic mixtures,[13] and a comparison has been made of the effects of different types of radiation on the aromatics.[12] An important feature in these systems is the migration of excitation energy from one molecule to another.

Studies on liquid scintillation counters have a close bearing on this subject. Certain solutions of aromatic compounds emit a large fraction of the absorbed energy as visible or ultraviolet light when they are irradiated with gamma rays. Practical development work on scintillation counters based on this phenomenon is proceeding at several laboratories.[49-52] A thorough study of the principles of energy transfer involved is being made by Kallmann[53] at New York University. Excitation energy has to migrate through several molecules in the solution before it can reach the particular molecule which is able to fluoresce. Kallmann's studies of light emission as a function of concentration in these solutions are of great value in understanding at least one feature of the mechanism of radiation damage in liquids.

Studies of the nature of the free radicals formed in radiolysis of some simple organic compounds have been carried out by Hammill and Williams[54] at Notre Dame, using a novel technique involving radioiodine in identification of the radicals. This technique should prove valuable in future studies along this line.

Malcolm Dole has initiated a study of the mechanism of the action of radiation on plastics.[55] However, this has constituted only a minor part of a far-reaching program which Dole hopes to carry out on the structure and properties of high-polymeric substances. Results to date have shown that polyethylene behaves toward radiation very much like the paraffin hydrocarbons. It is to be hoped that Dole will wish to continue with this aspect of his studies, which should complement the more empirical plastics testing which O. Sisman is carrying on at Oak Ridge.

Mention might be made here of the work of E. Pollard's group at Yale University on the inactivation of dry enzyme preparations by the cyclotron beam.[56] He has shown that nearly every time a deuteron passes through a gigantic molecule like pepsin the whole molecule is destroyed as far as its enzymatic activity is concerned. This may imply that energy is rapidly spread over at least a large portion of this protein molecule before any bonds are broken. Such information, though obtained solely for its interest in radiobiology, is important in the consideration of effects on materials generally.

3. Aqueous Solutions. The major portion of the work currently being published on radiation chemistry seems to involve the effect of X rays or gamma rays on aqueous solutions. One reason for the activity in this field is the belief that the phenomena of radiobiology are to be ultimately explained in terms of solution reactions.[57] The same subject is of concern to reactor designers in connection with aqueous homogeneous reactors and other types of reactors in which water is used as a coolant or heavy water is used as a moderator.

In this field of radiation chemistry the details of the initial excitation processes occurring in the water may be largely ignored because the

DECLASSIFIED

final result of all such processes is believed to be simply the dissociation of water to the free radicals[11] H and OH. The observed reactions can then be interpreted in terms of the subsequent behavior of these radicals.[58]

Water decomposes readily when irradiated with heavy-particle radiations of high ionization density, such as alpha rays or fission recoils, the products being oxygen and hydrogen gases and, at ordinary temperatures, hydrogen peroxide, which remains in solution. The peroxide probably is formed initially by the reaction

$$2H_2O \rightarrow H_2 + H_2O_2$$

and oxygen appears, mostly or entirely, as a secondary product from the subsequent partial decomposition of the peroxide

$$H_2O_2 \rightarrow H_2O + \tfrac{1}{2}O_2$$

X rays, gamma rays, or electrons give very little decomposition of water. The decomposition proceeds to a very small extent and then reverses itself, so that under irradiation a steady state is soon reached in which only a very small amount of hydrogen is present.[58] In aqueous solutions all organic and many inorganic solutes even at high dilution (10^{-4}M) show oxidation and reduction reactions with yield values (based on total energy absorbed by the solution) of the order expected for pure materials, so that a large percentage conversion of the dissolved material may be obtained with total doses which would produce no observable decomposition on pure materials.[57] The explanation is that the radicals formed by the dissociation of the water diffuse through a solution and react with the dissolved materials. When pure water is irradiated, the oxygen, hydrogen, and peroxide produced by water decomposition are soon attacked by the radicals and are thereby reconverted to water, so that very little net decomposition results. To explain the continuing decomposition from the alpha rays and fission recoils, it must be assumed that the radicals are initially formed so close together in the radiation tracks that nearly all of them react with one another to form the decomposition products, so that very few radicals escape into the solution[59] to bring about recombination of the hydrogen and oxygen to water. Irradiated water thus behaves as though two simultaneous reactions were occurring. The reaction

$$2H_2O \rightarrow H_2 + H_2O_2$$

appears to be occurring in regions of high ionization density, whereas the reaction

$$H_2O \rightarrow H + OH$$

symbolizes the formation of free radicals and their subsequent escape by diffusion into the body of the solution. A quantitative study of the decomposition of water under reactor radiation and the back reaction of the products H_2 and H_2O_2 has been described in the literature.[60] For the case where excess hydrogen was present, a simple scheme of subsequent reactions between the radicals H_2 and H_2O_2 was sufficient to describe the experimental results quantitatively. When peroxide or oxygen was in excess, the results were not very reproducible, and it was concluded that the subsequent reactions of the radicals were more complicated. The results show definitely that water decomposition is inhibited by excess hydrogen and favored by excess oxygen or peroxide.

Many papers have been published on X-ray effects in aqueous solutions, and much work is still being done in this field. Oxidizing agents are reduced,[61] reducing agents are oxidized,[62] and organic substances in solution are decomposed, usually with the formation of hydrogen and carbon dioxide.[63] The yields obtained[63] differ for different compounds and, in general, are likely to vary quite a bit with changes in pH. Although in all solutions the same number of radicals must be produced from the water by a given dose of radiation, the yields vary in different cases because the oxidizing and reducing radicals OH and H are formed simultaneously, and whatever reaction may be brought about by one can be reversed by the other. This reversal must proceed to a different extent with different solutes, depending upon the specific rates of the different free-radical reactions involved. The total number of radicals produced in water by a given expenditure of energy is thus still not firmly established, although attempts are being made to establish this number by a study of the mechanisms of appropriate solution reactions.[64,65] The mechanisms of all these reactions

714 173

~~237 010~~

are complicated by the formation of molecular H_2 and H_2O_2, which continues to occur in the solutions along with formation of free radicals. The oxidation in air-free solutions of a considerable number of inorganic reducing agents was found by Fricke and Hart[62] to proceed at the same relatively low yield value; this value is taken to represent the yield of H_2O_2 formed by direct water decomposition.[58] The H_2O_2 subsequently reacts with the dissolved reducing agent (this reaction perhaps being catalyzed by the presence of the radicals), whereas the bulk of the free radicals produce oxidation and reduction in the solution in equivalent amounts and hence give no net effect.

When more than one solute is present, the more reactive one will react with radicals in preference to the other; the more reactive solute is destroyed, and the less reactive solute, which would be destroyed in the absence of the first, is said to be "protected."[66] The decomposition of water observed in solutions of such active solutes as bromide ion or copper ion is an example of protection. The water-decomposition products in this case are protected; they do not revert back to water because the radicals which would otherwise bring about this reaction are used up by reaction with the added solute. For this reason decomposition of water under reactor radiation may be greatly increased by the presence of traces of impurities, such as bromide ion, copper ion, or even dissolved glass.[60] By systematic studies of the protection effect, the relative rates of reaction of radicals with different substances can be determined.[66]

The aims in current studies of radiation chemistry of solutions are (1) to discover the nature and rates of reactions of free radicals with solutes of various kinds, (2) to use this information to determine the number of free radicals formed by radiation in water and to deduce their initial distribution and subsequent diffusion behavior for radiations of various mean ionization densities, and (3) to use the results in interpreting what appears when living things are irradiated or when water or aqueous solutions are used in reactors.

Studies along these lines are under way at all the AEC national laboratories. At the Chemistry Division of the Argonne National Laboratory, E. J. Hart has been studying the mechanism of decomposition of aqueous formic acid in both the presence and absence of oxygen and hydrogen peroxide and has obtained a number which he thinks may represent the absolute number of radicals produced in the water.[64,65,67] He has also studied the oxidation of ferrous sulfate in aerated and air-free solutions[68] and has obtained some results which do not altogether agree with those of Krenz and Dewhurst,[69] who have made a long investigation of the same reaction at Chalk River and at the University of Edinburgh, Scotland. Sheffield Gordon, working with Hart, has been studying the rate of exchange between deuterium and water under gamma rays and has obtained some interesting results on the pH dependence of the yield. However, as yet these results have not been fully explained.[68]

At Brookhaven, Everett Johnson, working with the author, is studying mechanisms of peroxide decomposition and hydrogen formation in water and solutions of bromide.[70] At Oak Ridge, C. J. Hochanadel is studying the kinetics of the reaction between hydrogen and hydrogen peroxide in solution under gamma rays and related reactions.[64,65] Progress in these studies is perhaps not too rapid because of the care required in the preparation of absolutely clean and pure air-free solutions and because of the laborious processes of gas analysis which are necessary to determine completely the nature of the reactions occurring.

In the Biology Division at Argonne, Barron[71] has published a long series of papers on X-ray effects in solutions of enzymes and other materials of biological interest. He is currently interested in a study of the oxidation of glutathione and its effects on cytochrome. From yields obtained in aerated solutions, air-free solutions, and solutions to which catalase is added, Barron[72] believes he has obtained the contributions to the reactions on the substrate of the entities OH, HO_2, and H_2O_2, respectively. Pomeroy has been studying the yields of destruction of stable free radicals, such as dipicrylhydrazyl, in the hope of obtaining a measure of the number of free radicals formed.[73] It is hoped that he will proceed on this laudable project in the face of the great chemical complications. Solon Gordon, of the Biology Division at Argonne, has been irradiating solutions of indoleacetic acid.[74] The disappearance of this material is an exponential function of the time of irradiation instead of the linear function which is attained with simpler molecules. The exponential rela-

DECLASSIFIED

tion is always found with very large molecules, such as enzymes, and is taken to mean that a molecule deactivated by radiation is just as active chemically toward radicals as before its deactivation.[57] Further work on the mechanism of the indoleacetic acid reaction should be instructive.

In the Biology Department at Brookhaven, Nims and Scheraga[75] are studying the effects of X rays on fibrinogen solutions.

At Canisius College, Schuler[76] is studying the mechanism of the radiation decolorization of dye solutions, which also show exponential reaction-dose curves.

Toulis working with Tobias in the Department of Medical Physics, UCRL, made a study of the decomposition of water by cyclotron radiation,[77] but no further work on these lines is planned at that laboratory. Garrison and coworkers[78] are studying the reduction of carbon dioxide in irradiated solutions, in the hope of shedding some light on the problem of how life originated in the primeval oceans.

From the AEC project at the University of California at Los Angeles, a study has appeared of chemical changes occurring on the irradiation of dilute solutions of the cysteine.[79]

Work on reaction mechanisms in irradiated aqueous solutions, similar to that mentioned above, is proceeding actively in Europe. In France, Lefort and Bonét-Maury have published several papers on the decomposition of water and the formation of peroxide in solutions irradiated with X rays and alpha rays.[80-82] In England, Weiss, Stein, and Day are studying the formation of phenols in irradiated aqueous solutions of benzene and benzoic acid in the hope of shedding new light on the reactions of OH radicals.[83,84] F. S. Dainton, now at Leeds, became interested in radiation chemistry at Chalk River during the war and published some work on the polymerization of acrylonitrile solutions. He hoped to determine the total number of radicals formed by the determination of the number of combined OH groups in the polymer.[11] He is said to be continuing these studies and initiating others in this field. Amphlett,[85] at Harwell, has been studying the role of complexes in the study of kinetics of radiation reactions of metal salts in solution.[85] A group at Edinburgh, including N. Miller, F. H. Krenz, and H. Dewhurst, all formerly of Chalk River, are studying the mechanism of the ferrous sulfate oxidation and are also interested in radiation-induced polymerizations.[86] Interest in radiation chemistry seems quite widespread among British physical chemists, and the discussion of the Faraday Society in the spring of 1952 will be devoted to radiation chemistry.

Robley Evans and C. J. Maletskos, at MIT, are studying the possibilities of using magnetic or optical methods to obtain a direct measure of the lifetimes of free radicals in irradiated water.[87] This lifetime should, of course, depend on the rates of the chemical reactions of the radicals.

All these studies of free-radical behavior in irradiated solutions can be usefully supplemented by studies of free radicals (presumably the same radicals) formed in aqueous solutions in other ways. To this end, Dainton has studied the photolysis of hydrogen peroxide solutions and is making a study of other ways in which free H or OH may be generated in water.

The OH radical is supposed to be generated when hydrogen peroxide reacts with ferrous sulfate in aqueous solutions. If organic materials are added to the solution, they are oxidized by these radicals, and useful polymerizations may be induced in this way. This oxidation reaction of organic substances is called the "Fenton reaction," and detailed studies of the mechanism of this reaction are being made by a group at Leeds, including Evans and Baxendale,[88,89] by Waters at Oxford,[90] and by Medalia at Brookhaven.[91-93] Studies of the polymerizations induced in this way are probably going on at a number of industrial laboratories; there are recent publications by Williams of the Polymer Corporation, Ltd., Sarnia, Ontario.[94] Work on the Fenton reaction is of great interest to radiation chemists.

There has been a recent revival of interest in the use of chemical reactions as radiation dosimeters. The emphasis has been on finding reactions in which a large, evident change in some property is produced by a small dose. On irradiation, solutions of chlorinated organic compounds exhibit chain reactions which result in large yields. Taplin,[95] of the AEC project at UCLA, has proposed a chloroform-water mix-

714 175

237 012

ture as a dosimeter; a group at Bethesda prefers chloral solutions.[96] Davis,[97] at New York University, is studying the Eder reaction induced by gamma rays. This is a very long chain reaction involving the reduction of mercuric chloride with oxalate to calomel. Turbidities are produced by doses of only a few roentgens, but the yield is not reproducible.

Reactions induced in tritium water by the tritium radiation are of interest at Los Alamos Scientific Laboratory and at the Knolls Atomic Power Laboratory. Challenger and Rollefson have published a paper from Los Alamos in which the kinetics of the reduction of ceric sulfate in tritium water are reported.[98] Dorfman, at Knolls, is studying the combination of tritium and oxygen. Studies of tritium water are of particular interest since the mean density of ionization by the slow tritium betas is intermediate between the ionization densities of fast electrons or X rays and the heavy-particle radiations usually employed in radiation chemical studies. Hart has been using tritium in this way to supplement his studies of gamma rays on formic acid and ferrous sulfate solutions.[67]

4. Decomposition of Salts. Many solid salts containing covalent bonds, such as nitrates, bromates, chlorates, etc., decompose under high-energy radiation. Very little systematic work has been done on this subject.

Chlorates also decompose, but iodates do not. Boyd, at Oak Ridge, has studied radiation decomposition of bromate and other solid salts in connection with studies on the nuclear activation of bromine.[100] Davis, at NYU, has been interested in radiation decomposition of nitrates[97] but is not continuing these studies at the present time. This interesting field deserves further study.

Materials Testing and Development

Every reactor-design project has always included a few tests of the effects of radiation on miscellaneous materials, such as plastics, oils, and ceramics. These tests have usually been sporadic and have often been done by people who had no interest in developing a more systematic knowledge of the subject, and the results are either not reported at all or are mentioned only briefly in progress reports, where they are difficult to find. Such tests have often proved meaningless because the conditions of the test were not well enough controlled or significant properties of materials were not measured. A review by Richardson and Allen[101] of random tests made on plastics in the Oak Ridge reactor, in the earlier days of its operation, revealed that much of the deterioration reported must have resulted from the high temperature of the reactor rather than from the radiation, to which the effects had been wrongly attributed.

The effects of reactor radiation on plastics of various kinds is now, however, being studied very thoroughly and systematically at Oak Ridge by Sisman.[102] A large number of mechanical and electrical properties are being investigated as functions of the amount of reactor radiation received when the temperature of the specimens is controlled. Some interesting correlations have already emerged between radiation resistance and such characteristics of the plastic as the aromatic nature of the material, the character and amount of filler, and the amount of cross linking. Inorganic-filled phenolic plastics seem to stand up by far the best. The program could be greatly extended in the directions of studying effects of different kinds of radiation, the effects of temperature, and more elaborate studies of electrical properties, during, as well as after, irradiation. As far as the author is aware, no attempts are under way to develop new plastics from the standpoint of radiation-damage resistance.

Damage to lubricating oils has been the subject of a thorough, systematic study undertaken for Fairchild Engine & Airplane Corp. (NEPA) by the California Research Corporation.[103] Here the purpose was not only to test existing materials for radiation resistance but also to develop new oils which would be more radiation resistant than any existing. A large amount of data was obtained systematically on the change in viscosity of various oils with the amount of radiation received in the Oak Ridge reactor. Results showed that incorporating aromatic rings in the oil greatly improved radiation resistance, and the addition of a few per cent of certain compounds of iodine caused a further large increase in radiation resistance. The project is currently being continued under contract with the AEC

DECLASSIFIED

Reactor Division. The California people realize the utility of the cyclotron and Van de Graaff generator radiations for damage testing and will probably find that such bombardments will prove more useful than the Hanford reactor exposures which they currently have under way. This program is by far the best that has yet been carried out in the field of materials testing and development for radiation resistance.

Some materials testing with gamma rays is going on at Westinghouse Electric Corp. and General Electric Company but on a smaller scale and less systematically than the two projects mentioned above.

Studies of possible uses for high-energy radiations have been carried on for some time by Trump, Proctor, and others at MIT interested in the utilization of cathode rays from the Van de Graaff machine[16,104] and by Brasch and associates (see references 19, 20, 105-108), interested in the application of cathode rays from the capacitron. Both groups apparently soon came to the conclusion that the biological field was the most fruitful. The reason for this is that much lower doses are required to damage living things than are needed to affect inanimate materials. Sterilization of foods and drugs, killing weevils and their eggs in wheat, embalming, etc., seem to be the most probable uses of radiation in the near future.

Possibilities of chemical syntheses by radiation are being explored by Williams and Manowitz, of Brookhaven. Good polymers can be made by radiation from such materials as methyl methacrylate, but the advantage of this method over conventional polymerization methods is not obvious. Brownell and Meinke, at Michigan, are interested in using radiation for food preservation and for improving the performance of jet and internal-combustion engines. Selke, at Columbia, is interested in radiation synthesis of ammonia and hydrazine, and Bretton, at Yale, proposes to study uses of gas-phase chain reactions initiated by radiation, such as the reactions of acetylene. The use of intense radiation sources to modify and improve the characteristics of the electric discharge in ammonia (used for hydrazine production) is under study by Akerlof at the Navy laboratory at Indian Head.[109] Another suggested use is the modification of catalytic properties of solid catalysts by irradiation. Taylor and Wethington are looking into this subject at Oak Ridge.[110] Certainly some use should be found for the tremendous quantities of fission products soon to be available, but as yet no clear line of development has emerged, except in the field of food and drug preservation.

Reactor-component Testing

1. Homogeneous Reactor Experiment (HRE) at Oak Ridge. Problems of radiation chemistry are supposed to be especially serious in this reactor. Basic work on the decomposition of water by fission recoils had been done at Oak Ridge by Shapiro and Boyle in the past.[111] The experiments showed that water containing dissolved uranium or plutonium undergoing fission decomposed with a yield of 2 molecules per 100 ev of fission-recoil energy expended. The products, H_2 and O_2 gases with some H_2O_2, did not recombine to form water under the radiation even at pressures of hundreds of atmospheres. Uranium precipitated as the peroxide, UO_4, in neutral solution, but the addition of acid prevented this precipitation. In uranyl sulfate solution containing H_2SO_4, the uranyl and sulfate ions were apparently unaffected by radiation since only the water decomposed.

At present, gas production is taken for granted; provision is made in the HRE for the removal and recombination of the gases, and gas bubbling is no longer believed to offer a very serious problem in reactivity control.[112] Attention is centered on the problem of the corrosion of metal containers by uranyl sulfate solutions at the high temperature proposed (250°C). Radiation has been shown not to accelerate this corrosion, and in fact some indications have appeared that radiation may help to protect the metal against corrosion. The biggest problem in the HRE at present is not radiation damage but is a corrosion problem which has little to do with radiation.

The stability of uranyl and sulfate ions in irradiated solutions is in accord with the oxidative character of irradiated solutions containing oxygen. The reducing radical H readily combines with O_2 to yield the radical HO_2, an active oxidizing agent, so that all radicals present are oxidizing. It is presumed that whenever UO_2^{++} and SO_4^{--} are broken up by radiation the uranium and sulfur are quickly oxidized back to their original states by free radicals. With nitrate

DECLASSIFIED

the situation may be less favorable. Data from Los Alamos, quoted by Mills,[113] show considerable quantities of nitrogen coming from highly concentrated solutions of uranyl nitrate undergoing fission. Stability of nitrate ion in dilute solutions is now being studied at Oak Ridge. There is no reason to expect that the hydrogen and oxygen yields under fission will differ much in dilute nitrate and dilute sulfate solutions, despite Mills's statements.

2. Other Homogeneous Reactor Systems. Aqueous uranium oxide slurries were under consideration for homogeneous reactors at the Metallurgical Laboratory in 1944, and interest in this type has recently been revived. However, no actual radiation tests have ever been made on such a system.

Fused uranium fluoride mixed with other fluorides is another proposed fuel for homogeneous reactors. A preliminary test indicated no radiation decomposition of the fluoride mixture, but further experiments are clearly indicated.[114] Unfortunately no background information exists at all on the chemical effects of radiation on simple fused salts.

Slurries of uranium oxide in fused sodium hydroxide are another proposed homogeneous reactor fuel. Fused sodium hydroxide has been shown at NEPA to decompose little or not at all under intense cathode-ray bombardment.[115] The effect of fission in an actual slurry has not yet been tried.

In any homogeneous reactor the fluid medium is penetrated directly by fission recoils. The ionization density in the tracks of these particles is an order of magnitude greater than for any other known radiations; therefore their effects cannot be adequately simulated. In water solution, the only system as yet thoroughly studied, the effect of fission recoils seems to be different from that of other radiations in that a radiation-induced back reaction between the decomposition products to re-form water does not occur, even at very high product-gas pressures. Tests thus have to be made with actual fissions, which means exposing fuel materials in reactors. Because of handling difficulties, such tests are bound to be time consuming and expensive.

In the absence of experimental data on fused halides, the main effect of radiation may be presumed to be the transfer of an electron from a negative to a positive ion, giving neutral atoms, as $Na^+ + F^- \rightarrow Na + F$. The resulting metal and halogen will recombine spontaneously and very rapidly to give the original salt; therefore no net observable effect is expected. However, under turbulent-flow conditions the free halogen might sometimes come into contact with the wall and react with it before it has time to meet and react with the free metal atom, thereby producing corrosion. Thus observed radiation stability in static tests does not necessarily prove the absence of radiation-induced corrosion in a dynamic system.

The effect of radiation on sodium hydroxide slurry is also an unsolved problem. Of the possible NaOH decomposition reactions, the only one which is not spontaneously reversible would seem to be the decomposition to H_2 and O_2 gases and Na_2O. Stability under cathode rays indicates that this reaction may be unimportant, but by analogy with water we might expect the decomposition to gases to be more prominent with fission recoils than with cathode rays. Also, the presence of uranium might have an unfavorable chemical effect, as in the case of anhydrous H_2SO_4. This acid when pure is little affected by radiation, but in the presence of dissolved hexavalent uranium much decomposition[116] occurs to SO_2 and O_2. Presumably in the pure liquid any SO_2 formed is quickly reoxidized by free radicals, but the uranium ties up the radicals in some way thus allowing the SO_2 to escape. The effect is analogous to the increase in water decomposition caused by impurities under fast-neutron irradiation. Such effects should be looked for in NaOH.

Occurrence of fission in the small oxide particles of a slurry might also produce effects on the size and character of the particles themselves. Such effects have often been talked about but have never been studied experimentally.

To form a stable slurry at all is a complex problem upon which much effort has been expended. The particles must be small enough so that they will not settle out, and they cannot be allowed to grow with time by recrystallization. They must be soft enough so that they do not erode the containing pipes when circulated at high velocity. Uranium forms several oxides, not all of which form satisfactory slurries. Whether a given lot of oxide will disperse properly in water depends on the details of preparation of the oxide, such as amount of oven-drying

DECLASSIFIED

and the presence of trace impurities of electrolytes such as uranyl nitrate.[117] The surface condition of the particles is evidently of importance. Radiation will have some effect here by altering the chemical nature of the environment (which may be a great enough effect to oxidize the whole particle) as well as by affecting the structure of the particle by internal fissions. The variables involved are so complex that long series of empirical irradiation tests on slurries would be necessary to develop a satisfactory slurry reactor. Because of handling difficulties arising from the high fission-product-radioactivity level, these tests would be unusually prolonged, difficult, and expensive.

A solution of uranium in liquid metal offers a homogeneous fuel possibility which could hardly be subject to any conceivable radiation damage. The proposal,[118] currently being studied at Brookhaven, for circulating a solution of uranium metal in liquid bismuth is certainly far superior to other homogeneous proposals from the standpoint of radiation-damage problems.

3. Separation Processes. The separation of fission products and plutonium by solvent extraction might conceivably be affected by radiations from radioactive materials contained in the solution. Radiation levels in these solutions are generally not high enough to produce important amounts of chemical change in the time intervals involved. Testing of such effects can be made conveniently either by using actual fission products as an internal radiation source or by using an external source such as a Van de Graaff machine. These tests have, in the past, always yielded negative results;[119] i.e., the radiation levels have not been high enough to cause any trouble. A recent problem in this field concerns the proposed use of carbon tetrachloride in the Purex process of solvent extraction. It is feared that radiation might cause hydrolysis of carbon tetrachloride, resulting in the appearance of chloride ion in the acid aqueous phase, with the resulting danger of corrosion.[120] This suspicion seems well founded enough to warrant a study of the amount of chloride ion produced by radiation on the system in question. This type of problem will not, in general, become of major importance unless proposals are made to operate extraction processes at very much higher radiation levels than hitherto contemplated. Such a proposal is now under consideration at North American Aviation, Inc., and appropriate radiation tests are planned.[121]

FUTURE INVESTIGATIONS AND RECOMMENDATIONS

Basic Research

The foregoing review has shown that fundamental study in the field of radiation chemistry is supported by the AEC to a greater extent than many people are probably aware. Considerable interest in the field also exists outside the AEC, and it is, in fact, a small but active and rapidly growing field of physical chemistry.

Research on reaction mechanisms in aqueous solution is flourishing at all three national laboratories and in other laboratories in this country and abroad. Emphasis is being placed right now on reactions induced by X rays and gamma rays. This is probably because such reactions are easier to study and interpret than those induced by radiations of higher ionization density. Current researches are reaching the stage in which a real understanding of some of the reactions induced by gamma rays may be said to be in sight, and it can be argued that detailed work in this field with other types of radiation may well be postponed until a better understanding of the gamma-ray mechanisms is achieved. However, further exploration of the influence of ionization density of radiation on the mechanism of some reactions would not be amiss at this time, and program planning in this direction should be encouraged.

The topic in the aqueous field on which fundamental knowledge seems to be most lacking at present is the decomposition of water by fission recoils. The radiation chemists at Oak Ridge, who understand best the very difficult techniques involved in the study of this problem, seem to be currently sidetracked into a study of corrosion effects in the HRE. Fission recoils are so intensely ionizing that probably all water molecules lying in the immediate neighborhood of the particle track will dissociate. Whether any free radicals manage to escape from this region of extremely high concentration is not known; the problem is obscured by the unavoidable presence of gamma rays in the solution and by the chemical effects of the uranium which is always present. The stability of various substances such as

DECLASSIFIED

nitric acid in the presence of fissioning uranium in solution has not been adequately studied and is difficult to predict with certainty. Basic researches on this topic might not have much direct influence on the development of homogeneous reactor systems, but they are well worth while in extending our knowledge of the processes occurring in such reactors.

The organic field is less popular than the aqueous field because the reaction products are always much more complicated and more difficult to study. Much needs to be done in these systems, both on the lines of detailed analysis of the products of irradiation of simple pure compounds, as in Newton's work, and on the lines of studying effects in mixtures to gain insight into the processes of the intermolecular transfer of energy, as in some work of Burton. Progress in this field cannot be expected to be rapid, and anyone disposed to enter this difficult field of work should be encouraged. Practical developments in the field of radiation effects in organic compounds must, in the long run, depend upon maintaining a background of fundamental work in that field.

Basic work in the field of radiation chemical effects in salts is very slight. Homogeneous-reactor designers are particularly interested in fused salts. To the best of the writer's knowledge, very little information is available on fused salts, with respect either to radiation chemistry or to any other physical or chemical properties. Intelligent study of the effects of radiation on these materials can hardly be made without a more complete knowledge of their normal structure, chemical behavior, and electrical properties. It would seem most appropriate to develop and undertake a broad research program in the physical chemistry of fused salts, with the effects of radiation constituting but one small aspect of this study.

The study of radiation decomposition in solid salts constitutes a promising field at the present time in which work should be pushed. Enough is known about the structure and electrical behavior of solid salts so that some reasonable degree of understanding of their radiation chemistry should be possible.

Materials Testing and Development

It is this field in which coordination and direction have been particularly lacking and in which efforts to develop a program could be most usefully expended. Fundamental research in reaction mechanisms or in any other field is a delicate thing and difficult to stimulate artificially, but a well-rounded and comprehensive study of materials testing fills an obvious need and could be readily effected simply by an effort at the organization and coordination of those interested. The efforts of the California Research Corporation on oils and Sisman's group at Oak Ridge on plastics offer a good beginning. Many other people would presumably be glad to participate if a wider program along these lines were formulated and competently coordinated. The Oak Ridge work on plastics could be extended to cover different types of radiations on the same materials; samples and testing methods could be standardized by the different laboratories, and a sensible picture of the radiation resistance of plastics would soon emerge. The efforts of the California Research Corporation on lubricants could similarly be increased by the participation of cooperating laboratories.

The effects of radiation on glass and ceramics should be similarly studied by a concerted attack. Little is known about the resistance of glass to radiation because few systematic studies have been attempted. It has been stated that glass vessels used to contain substances which emit alpha rays become weakened by the bombardment; on the other hand, glass vessels have been exposed in the Oak Ridge reactor for weeks without apparent weakening. Effects of radiation on the electrical conductivity of glass or ceramic insulators seem likewise not to have been subjected to any systematic study. Systematic programs along these lines could be initiated. The experiments would be simple and not too expensive, and the results, if properly coordinated and disseminated, would be of great use to reactor designers.

REFERENCES

1. F. Rasetti, "Elements of Nuclear Physics," Prentice-Hall, Inc., New York, 1936.
2. E. Pollard and W. L. Davidson, "Applied Nuclear Physics," 2d ed., John Wiley & Sons, Inc., New York, 1951.
3. E. Rutherford, J. Chadwick, and C. D. Ellis, "Radiations from Radioactive Substances," Cambridge University Press, London, 1930.
4. F. Seitz, "The Modern Theory of Solids," McGraw-Hill Book Company, Inc., New York, 1940.

714 180
037 017
DECLASSIFIED

5. F. Seitz, Faraday Soc. Discussions, 5: 271 (1949).
6. J. A. Hipple, J. Phys. & Colloid Chem., 52: 456 (1948).
7. H. Eyring, J. O. Hirschfelder, and H. S. Taylor, J. Chem. Phys., 4: 479 (1936).
8. L. B. Loeb, "Fundamental Processes of Electric Discharge in Gases," p. 71, John Wiley & Sons, Inc., New York, 1939.
9. L. B. Loeb, "Fundamental Processes of Electric Discharge in Gases," Chap. VI, John Wiley & Sons, Inc., New York, 1939.
10. "Handbook of Chemistry and Physics," Chemical Rubber Publishing Co., table of Ionization Potentials, Compounds.
11. F. S. Dainton, J. Phys. & Colloid Chem., 52: 490 (1948).
12. T. J. Sworski, Thesis, University of Notre Dame, 1951; T. J. Sworski and M. Burton, J. Am. Chem. Soc., 73: 3790-3792 (1951).
13. J. P. Manion and M. Burton, paper presented at American Chemical Society Meeting, Cleveland, Ohio, April 1951.
14. M. Goldberger, R. J. Stephenson, and A. M. Weinberg, Report CP-2439, Nov. 30, 1944.
15. D. M. Richardson, Report ORNL-129, 1948.
16. J. G. Trump and R. J. Van de Graaff, J. Applied Phys., 19: 599 (1948).
17. E. J. Hart, The Effects of Ionizing Radiations on Aqueous Solutions of Organic Acids, TID-272, p. 69.
18. J. A. Ghormley and C. J. Hochanadel, Report ORNL-897, Feb. 6, 1951.
19. A. Brasch and W. Huber, Science, 105: 112 (1947).
20. W. Huber, Electronics, March 1948.
21. S. C. Lind, "The Chemical Effects of Alpha Particles and Electrons," 2d ed., Chemical Catalog Company, Inc., New York, 1928.
22. W. Mund, "L'action chimique des rayons alpha en phase gazeuse," Hermann & Cie., Paris, 1935.
23. H. Eyring, J. O. Hirschfelder, and H. S. Taylor, J. Chem. Phys., 4: 570 (1936).
24. J. O. Hirschfelder and H. S. Taylor, J. Chem. Phys., 6: 783 (1938).
25. W. Mund, T. de Menten de Hornes, and M. van Meersche, Bull. soc. chim. Belges, 56: 386 (1947).
26. W. Mund, R. Lories, and P. Huyskens, Bull. classe sci., acad. roy. Belg., 34: 651 (1948).
27. C. H. Shiflett, M. E. Steidlitz, and W. Davis, Report K-738, 1951.
28. H. Eyring, paper presented at National Research Council Symposium on Radiobiology, Oberlin, Ohio, June 1950.
29. O. Schaeffer, J. Chem. Phys., 18: 1501 (1950).
30. P. B. Weisz, J. Phys. & Colloid Chem., 52: 578 (1948).
31. P. B. Weisz and W. P. Kern, Phys. Rev., 75: 899 (1949).
32. N. T. Williams and H. Essex, J. Chem. Phys., 16: 1153 (1948); 17: 995 (1949).
33. A. D. Kolumban and H. Essex, J. Chem. Phys., 8: 450 (1940).
34. C. Smith and H. Essex, J. Chem. Phys., 6: 188 (1938).
35. D. Fitzgerald and H. Essex, J. Am. Chem. Soc., 56: 65 (1934).
36. M. J. McGuinness and H. Essex, J. Am. Chem. Soc., 64: 1908 (1942).
37. B. Burtt, personal communication.
38. J. L. Magee and M. Burton, J. Am. Chem. Soc., 72: 1965 (1950).
39. G. Glockler and S. C. Lind, "The Electrochemistry of Gases and Other Dielectrics," John Wiley & Sons, Inc., New York, 1939.
40. C. W. Sheppard and V. L. Burton, J. Am. Chem. Soc., 68: 1636 (1946).
41. I. A. Breger and V. L. Burton, J. Am. Chem. Soc., 68: 1639 (1946).
42. C. W. Sheppard and W. L. Whitehead, Bull. Am. Assoc. Petroleum Geol., 30: 32 (1946).
43. C. W. Sheppard and R. E. Honig, J. Phys. Chem., 50: 144-52 (1946).
44. R. E. Honig and C. W. Sheppard, J. Phys. Chem., 50: 119 (1946).
45. I. A. Breger, J. Phys. & Colloid Chem., 52: 551 (1948).
46. V. L. Burton, J. Am. Chem. Soc., 71: 4117 (1949).
47. R. K. Wakerling, Report UCRL-1175, Mar. 12, 1951.
48. M. Burton, J. Phys. & Colloid Chem., 52: 564 (1948).
49. M. Ageno, M. Chiozzotto, and R. Querzoli, Phys. Rev., 79: 720 (1950).
50. G. T. Reynolds, Nucleonics, 6: 68 (1950).
51. G. T. Reynolds, F. B. Harrison, and G. Salvini, Phys. Rev., 78: 488 (1950).
52. R. F. Post, Phys. Rev., 79: 735 (1950).
53. H. Kallmann and M. Furst, Phys. Rev., 79: 857 (1950).
54. R. R. Williams and W. H. Hamill, J. Am. Chem. Soc., 72: 1857 (1950).
55. D. G. Rose, Doctoral Thesis, Northwestern University, June 1949.
56. E. Pollard, American Scientist, 39: 99 (1951).
57. D. E. Lea, "Actions of Radiations on Living Cells," Cambridge University Press, London, 1947.
58. A. O. Allen, J. Phys. & Colloid Chem., 52: 479 (1948).
59. W. M. Dale, L. H. Gray, and W. J. Meredith, Phil. Trans. Roy. Soc., A242: 33 (1949).
60. A. O. Allen et al., Report ORNL-130, Oct. 11, 1949; also paper presented at American Chemical Society Meeting, Cleveland, Ohio, April 1951.

DECLASSIFIED

61. G. L. Clark and W. S. Coe, J. Chem. Phys., 5: 97 (1937).
62. H. Fricke and E. J. Hart, J. Chem. Phys., 3: 596 (1935).
63. H. Fricke, E. J. Hart, and H. P. Smith, J. Chem. Phys., 6: 229 (1938).
64. E. J. Hart, paper presented at American Chemical Society Meeting, Cleveland, Ohio, April 1951.
65. C. J. Hochanadel, paper presented at American Chemical Society Meeting, Cleveland, Ohio, April 1951.
66. W. M. Dale, Biochem. J., 36: 80 (1942).
67. E. J. Hart, J. Am. Chem. Soc., 73: 1891 (1951).
68. J. R. Gilbreath and O. C. Simpson, Summary of Report for Period April to September 1950, Report ANL-4526, p. 81.
69. F. H. Krenz and H. A. Dewhurst, J. Chem. Phys., 17: 1337 (1949).
70. Quarterly Progress Report October 1 to December 31, 1950; Report BNL-93, March 1951, pp. 58-63.
71. E. S. G. Barron and V. Flood, J. Gen. Physiol., 33: 229-241 (1950) and earlier papers.
72. E. S. G. Barron and V. Bonzell, Report ANL-4467, June 8, 1950, and personal communication.
73. Quarterly Progress Report, Chemistry Department, Oct. 1 to Dec. 31, 1950, Report ANL-4488, March 1951, pp. 82-83.
74. W. P. Bigler, Quarterly Report, Dec. 1, 1949 to Feb. 28, 1950, Report ANL-4488, Mar. 17, 1950, pp. 65-68.
75. H. Scheraga and L. F. Nims, paper presented at American Chemical Society Meeting, Chicago, Ill., September 1950.
76. R. H. Schuler, paper presented at American Chemical Society Meeting, Cleveland, Ohio, April 1951.
77. W. J. Toulis, Report UCRL-583, 1950.
78. W. M. Garrison, D. C. Morrison, J. G. Hamilton, A. A. Benson, and M. Calvin, Report UCRL-1192, 1951.
79. M. Rotheram, N. Todd, and S. L. Whitcher, Report UCLA-119, 1951.
80. M. Lefort, Thesis, University of Paris, 1950.
81. M. Lefort and P. Bonét-Maury, Compt. rend., 226: 173 (1948); and M. Lefort and M. Haïssinsky, Compt. rend., 228: 313, 831 (1949); 230: 534, 1156 (1950).
82. P. Bonét-Maury and M. Lefort, J. chim. phys., 47: 179 (1950).
83. M. J. Day and G. Stein, Nucleonics, 8: No. 2, 34 (February 1951).
84. G. Stein and J. Weiss, J. Chem. Soc., 1949: 3245.
85. C. B. Amphlett, Nature, 165: 977 (1950).
86. F. H. Krenz, personal communication.
87. C. J. Maletskos, personal communication.
88. J. H. Baxendale, M. G. Evans, and G. S. Park, Trans. Faraday Soc., 42: 155 (1946).
89. W. G. Barb, J. H. Baxendale, P. George, and K. R. Hargrave, Nature, 163: 692 (1949); Trans. Faraday Soc., 47: 462 (1951).
90. J. H. Merz and W. A. Waters, J. Chem. Soc., 1949: Supplement 1, p. 15.
91. I. M. Kolthoff and A. I. Medalia, J. Am. Chem. Soc., 71: 3777, 3784 (1949).
92. A. I. Medalia and I. M. Kolthoff, J. Polymer Sci., 4: 377 (1949).
93. A. I. Medalia, unpublished work.
94. J. W. L. Fordham and H. Leverne Williams, paper presented at American Chemical Society Meeting, Cleveland, Ohio, April 1951.
95. G. V. Taplin and C. H. Douglas, Ra-Det, Vol. 3, 5: (May 1950).
96. H. L. Andrews and P. A. Shore, J. Chem. Phys., 18: 1165 (1950).
97. T. W. Davis, personal communication.
98. G. E. Challenger and G. K. Rollefson, paper presented at American Chemical Society Meeting, Cleveland, Ohio, April 1951; Report AECU-1187.
100. J. W. Cobble and G. E. Boyd, paper presented at American Chemical Society Meeting, Cleveland, Ohio, April 1951.
101. A. O. Allen and D. M. Richardson, Report CNL-16, 1948.
102. O. Sisman and C. D. Bopp, Report ORNL-928, June 29, 1951.
103. R. O. Bolt and J. G. Carroll, Report NPA-1844.
104. C. G. Dunn et al., J. Applied Phys., 19: 605 (1948).
105. U. Friedemann, F. B. Traub, and W. Huber, Federation Proc., Vol. 9, No. 1, March 1950.
106. A. Brasch, W. Huber, U. Friedemann, and F. B. Traub, Proc. Rudolf Virchow Medical Soc. in the City of New York, Vol. 8 (1949).
107. A. Brasch and W. Huber, Science, 108: 536 (1948).
108. W. Huber, paper presented at Symposium on Effects of Radiation on Biological Systems at Polytech. Inst. Brooklyn, Feb. 18, 1950.
109. B. Manowitz and others, personal communications.
110. J. A. Wethington, Report ORNL-685, 1950, p. 153.
111. J. W. Boyle, Report TID-272, pp. 9-21.
112. C. E. Winters and A. M. Weinberg, Report ORNL-730, July 6, 1950.
113. M. M. Mills, Report NAA-SR 31, Table 6, Dec. 7, 1949, p. 31.
114. V. P. Calkins and W. R. Grimes, papers presented at Fluid Fuels Development Conference, Oak Ridge, Tenn., Apr. 18, 1951.

DECLASSIFIED

115. W. Browning, personal communication; Report TID-5021, Paper 7.
116. J. W. Boyle and A. O. Allen, Report ORNL-155, 1948.
117. R. Bradt and G. R. Dean, Report CC-2095, 1944.
118. D. H. Gurinsky, I. Kaplan, F. T. Miles, C. Williams, and W. E. Winsche, Report BNL-105, Apr. 27, 1951.
119. J. P. McBride, C. J. Hochanadel, and A. O. Allen, Report Mon N-231, 1946.
120. R. C. Vogel, personal communication.
121. Milton Feldman, personal communication.
122. Quarterly Report Sept. 1 through Nov. 31, Report ANL-4537, 1950, pp. 56-59.
123. A. O. Allen, T. W. Davis, and C. J. Hochanadel, Report Mon C-390, 1947.

714 183

DECLASSIFIED

THE EFFECTS OF FISSION RADIATIONS ON LUBRICANTS AND LUBRICATION

By R. O. BOLT, J. G. CARROLL, and G. H. DENISON

California Research Corporation, Richmond, California

Report TID-5045 (Del.)

FOREWORD

In the initial phase, research was conducted on the general effect of fission radiations on organic liquids. For the most part small amounts of fluids were exposed in vented containers to combined reactor radiations, though in some cases alpha and gamma radiations were used alone. Factors such as dosage, flux magnitude, and operating temperature were investigated with organic fluids alone and in combination with various additives. The effects, under radiation fluxes, of oxygen, metallic surfaces, etc., entered the problem. In subsequent phases oxidation tests were conducted since oxidation plays a profound part in the deterioration of organic fluids in air. The major part of this functional test work was undertaken outside the reactor, but numerous supplementary and supporting tests were conducted in the presence of combined radiations. In general, all these oxidation experiments served as screening tests whereby unsatisfactory materials were eliminated from further consideration for use in the final evaluation tests in operating bearings, but the satisfactory materials were not graded as to expected service performance. In the final phase of the study the fluids which had evidenced the best resistance to reactor radiations, both in static and accelerated oxidation tests, were evaluated as finished lubricants in operating bearings. The effect of combined radiations on the lubrication process itself was also studied briefly in certain of these functional tests.

The functional test work, which is the most important from an engineering standpoint, is presented first. "Oxidation Tests" and "Bearing-Lubrication Tests" appear in the series as Parts I and II, respectively. "Static Irradiations" will appear as Part III. This is of more general interest to the chemist and deals with some effects of dosage, flux type and magnitude, and operating temperature on mineral oils and on many other types of organic fluids.

PART I. OXIDATION TESTS

ABSTRACT

These experiments were undertaken to evaluate the stability of organic fluids to reactor radiations and excess oxygen. The oxidative condition simulated that present in turbojet lubricating sys-

DECLASSIFIED

tems, where high-temperature air is present in excess. Many thermal-oxidation tests were conducted in the absence of radiations on selected base oils and base oil. Eleven in-pile experiments were then performed under comparable conditions on the most promising formulations. Oxidations of previously irradiated fluids were also conducted in the absence of radiations. The results observed are presented as they relate to the stability of various base oils, the effect of radiations, and the effect of additives.

Test Procedures

Two basic types of oxidation tests were used in the present work. The first employed the oxidation cell described in the American Society for Testing Materials (ASTM) Method D943-47T.[2] Oxygen at a rate of about 3 liters/hr was passed into the oil, which was contained in the large glass test tube fitted at the top with a water-cooled condenser. The flow of oxygen was held constant throughout the tests since it was not established that saturation with oxygen was maintained. The test temperature was 140°C, and tests were run both with and without the copper- and iron-wire catalysts of the ASTM method. This procedure was employed in thermal oxidations and subsequent in-pile oxidation tests, thus yielding comparative data with and without reactor radiations. In this work viscosity increase and acid formation were observed as a function of time and radiation dosage.

The second type of oxidation test used is particularly adapted to the use of small quantities. Oils which had been irradiated in the X-10 reactor were oxidized in a Zeitfuchs[3] viscometer tube in an oil bath maintained at 210°F. Oxygen was bubbled through the material in the tube, and it was necessary only to stop the flow of oxygen to run a viscosity determination directly. In this manner the thickening action of the oxidation could be followed closely. The unavailability of large quantities of irradiated oils made necessary the use of this small-scale test.

Thermal-oxidation Tests

Many different types of unirradiated base oils were tested by the modified ASTM method, both alone and with oxidation inhibitors known to be effective in these base materials in conventional practice. Only the combinations most resistant to thermal oxidation, as well as to combined radiations in static tests, were subsequently proposed for in-pile experiments. In these thermal oxidations the criterion of deterioration was the increase in acidity of the oil under test, since this was found to be more sensitive than viscosity increase. The "neutralization number" (milligrams of KOH per gram of oil) was chosen for the index of acidity. The induction period is defined as the time required to reach a neutralization number of 10. Differences in induction periods of less than 100 hr are not considered significant in these thermal-oxidation tests.

Approximately 175 individual tests were conducted in this phase of the work. Table 1.1 summarizes typical data on four of the more promising basic types of oils with several of the inhibitors used. The data indicate the tremendous importance of chemical additives in imparting thermal oxidative stability.

Iodobenzene and 1-methylnaphthalene are not commonly considered as oxidation inhibitors. There is, however, some evidence that these materials, particularly in combination with quinizarin, did increase induction periods. The most important reason why compounds of iodine and highly aromatic naphthalene derivative were employed was that they were shown to be beneficial in the static irradiation experiments. Quinizarin was added to the combinations because it was found that under conditions of the test this material protects metals, especially copper, from attack. Even so, it was observed that the copper began to darken after about 300 to 400 hr in the test. This, however, appeared to involve a thin coating which had no noticeable effect on the induction periods shown in Table 1.1.

1. Alkyl Aromatic Base Oil. Organic compounds of sulfur and selenium were the most successful in the inhibition of this type of base oil. In static irradiation experiments the selenide was somewhat more effective in preventing viscosity increase than the thiophosphate or the polysulfide. Thus it was preferred for in-pile oxidation work with this base oil.

DECLASSIFIED

Table 1.1 — Summary of Results of Modified ASTM Turbine Oil Oxidation Tests on Various Base Oils and Inhibitors in the Absence of Radiations (Test conditions: temperature, 140°C; copper- and iron-wire catalysts; oxygen flow, 3 liters/hr)

Additives	Induction period, hr*
Di(2-ethylhexyl) sebacate base oil	
None	20
2% 2,6-di(t-butyl)-4-methylphenol	100
2% zinc dibutyl dithiocarbamate	125
2% phenyl dibutyl dithiophosphate	200
2% dihexacosyl polysulfide	200
2% didodecyl selenide	650
4% didodecyl selenide	1300
10% didodecyl selenide	1300
6.5% didodecyl selenide	1350
4% didodecyl selenide and 1% zinc dibutyl dithiocarbamate	1700
4% didodecyl selenide, 0.5% zinc dibutyl dithiocarbamate, and 2% iodobenzene	2000
5% didodecyl selenide and 2% iodobenzene; blend saturated with quinizarin	2700
5% didodecyl selenide and 20% 1-methylnaphthalene; blend saturated with quinizarin	3400
5% didodecyl selenide, 20% 1-methylnaphthalene, and 2% iodobenzene; blend saturated with quinizarin	3500
Poly(propene oxide) base oil	
None	10
2% didodecyl selenide	25
2% phenyl dibutyl dithiophosphate	25
2% phenyl-alpha-naphthylamine	50
1% zinc dibutyl dithiocarbamate	75
2% *N*,*N'*-diphenyl-*p*-phenylenediamine	700
Poly(propene oxide)-B base oil	
None	10
2% dihexacosyl polysulfide	25
2% phenyl dibutyl dithiophosphate	50
2% mercaptobenzothiazole	200
4% didodecyl selenide	200
4% didodecyl selenide and 2% mercaptobenzothiazole	800
5% didodecyl selenide, 2% mercaptobenzothiazole, and 2% iodobenzene; blend saturated with quinizarin	1650
5% didodecyl selenide and 2% iodobenzene; blend saturated with quinizarin	1700
Mixed alkylbenzene (mol. wt. ≅350) base oil	
None	100
2% 2,6-di(t-butyl)-4-methylphenol	200
2% zinc dibutyl dithiocarbamate	350
2% dihexacosyl polysulfide	550
2% didodecyl selenide	600
2% phenyl dibutyl dithiophosphate	1550
5% didodecyl selenide and 2% mercaptobenzothiazole	2100
5% phenyl dibutyl dithiophosphate and 2% iodobenzene; blend saturated with quinizarin	2400
5% didodecyl selenide and 2% iodobenzene; blend saturated with quinizarin	>2450
5% didodecyl selenide, 2% mercaptobenzothiazole, and 2% iodobenzene; blend saturated with quinizarin	>2700

*Time for neutralization number (milligrams of KOH per gram of oil) to reach 10.

2. Polyether Base Oils. Both poly(propene oxide) (one ether and one hydroxyl end group) and poly(propene oxide)-B (one ether and one ester end group) were evaluated in the thermal-oxidation tests, and the results are summarized in Table 1.1. The poly(propene oxide) displayed poor inhibitor response. The diamine, the best of the possibilities studied, actually catalyzed thickening in the static reactor tests. Poly(propene oxide)-B was considerably more receptive to the action of inhibitors. The promising combinations with mercaptobenzothiazole gave unusually high viscosity increases in the static reactor tests despite the favorable induction periods in the thermal-oxidation tests. The selenide-quinizarin combination containing iodobenzene yielded the highest induction period and was subsequently chosen for reactor oxidation tests.

3. Aliphatic Diesters. The selenide, with an optimum concentration of between 2 and 4 wt. %, was by far the most effective oxidation inhibitor

DECLASSIFIED

in the di(2-ethylhexyl) sebacate base fluid. Combinations with 1-methylnaphthalene, iodobenzene, and quinizarin were particularly promising and were chosen for oxidation in the reactor. Combinations with zinc dibutyl dithiocarbamate were shown to yield precipitates in static irradiation tests and were thus discarded.

Table 1.2—Summary of Oxidation Tests in the X-10 Reactor (Test conditions: temperature, No. 1 at 80 ± 2°C; Nos. 2, 3, and 4 at 90 ± 2°C; all others at 140 ± 3°C. Flux, Nos. 1 and 2 at 76 per cent of maximum; all others at 85 per cent of maximum. Oxygen flow, 3 liters/hr for all tests.)

Test No.	Oil identity	Additive identity*
1	Alkylbenzene (mol. wt. ≅250)	2% O-1, 4% S-14
2	Octadecylbenzene	2% O-1, (5% more added during test)
3	Di(2-ethylhexyl) sebacate	5% O-1, 2% R-2, S D-2, 20% S-1
4	Poly(propene oxide)-B	5% O-1, 2% R-2, S D-2
5	Di(2-ethylhexyl) sebacate	5% O-1, 2% R-2, S D-2, 20% S-1
6	Poly(propene oxide)-B	5% O-1, 2% R-2, S D-2
7	Octadecylbenzene	5% O-1, 6% R-2, S D-2
8	Solvent-refined western paraffinic lube oil (150N)	5% O-1, 6% R-2, S D-2, 20% S-1
9	Octadecylbenzene	5% O-1, S D-2
10	Poly(propene oxide)-B	5% O-1, 2% R-2, S D-2
11	Di(2-ethylhexyl) sebacate	5% O-1, S D-2, 20% S-1

*Code: O-1, didodecyl selenide; R-2, iodobenzene; D-2, quinizarin (S for saturated, ~0.2 per cent maximum); S-1, 1-methylnapthalene; S-14, poly(lauryl methacrylate).

Accelerated Oxidation Tests in the X-10 Reactor

The best combinations of the various base-oil types and additives in both the thermal oxidations and the static irradiation tests were used for in-pile oxidation tests. Similar experiments were also conducted to confirm the effectiveness of the selenide oxidation inhibitor and the iodobenzene protective agent and to show the performance of the best compounded mineral oil developed in the research. Table 1.2 identifies the fluids oxidized in the reactor experiments.

In all the in-pile experiments the radiation dosage is expressed in integrated thermal neutrons per square centimeter. It is merely convenient to use this mode of expression, and it is not meant to imply that thermal neutrons cause the greatest amount of deterioration in the fluids. Indeed, it is probable that fast neutrons and/or gamma rays have a greater effect. Both gamma and fast-neutron dosages are of the order of one-tenth of the thermal-neutron dosages received by the samples in the reactor.[4-6]

1. Procedure and Apparatus. The in-pile procedure followed closely that of the thermal-oxidation tests except that temperatures of 80, 90, and 140°C were used. The two lower temperatures were obtained in hole 12, since this facility was cooled by a water jacket for which the maximum allowable temperature was about 90°C. The higher test temperature was obtained by placing the apparatus in a special heater in hole 54N. High-flux (75 to 88 per cent maximum) positions were utilized in both these facilities.

The oxidation cell used for the tests consisted basically of an aluminum cylinder with a 2$\frac{1}{16}$-in. I.D. and 275-ml volume. The cell was heated, in the 140°C experiments, by means of nichrome wire insulated from the metal with alundum beads, and the assembly was enclosed in a sheet-aluminum box. Inlet and outlet lines of aluminum, thermocouples, and aluminum heater leads extended from the cell in the reactor to the control apparatus outside.

After placement in the reactor, the cell was charged by introducing ~150 ml of the test fluid through the inlet tube. Oxygen at the rate of 3 liters/hr was then bubbled through the oil by the use of the same tube. Exhaust gases passed through a liquid trap (an alkaline scrubber) and were then vented to the reactor air stream. Periodic samples of the test oil were taken by reversing the oxygen flow so that the oil was forced out the normal inlet tube under slight pressure. Plumbing arrangements were such that oxidized samples could be removed, the cell could be flushed with a suitable solvent, the excess solvent could be removed by flushing with nitrogen, and a new sample could be introduced for subsequent oxidation. Catalysts were placed in the cell in the first in-pile experiment but were omitted in later experiments when it was found that they had little effect on viscosity increase in this type of test. The absence of catalysts facilitated the reuse of the apparatus for repeated oxidation experiments without removal from the reactor after each test in the series.

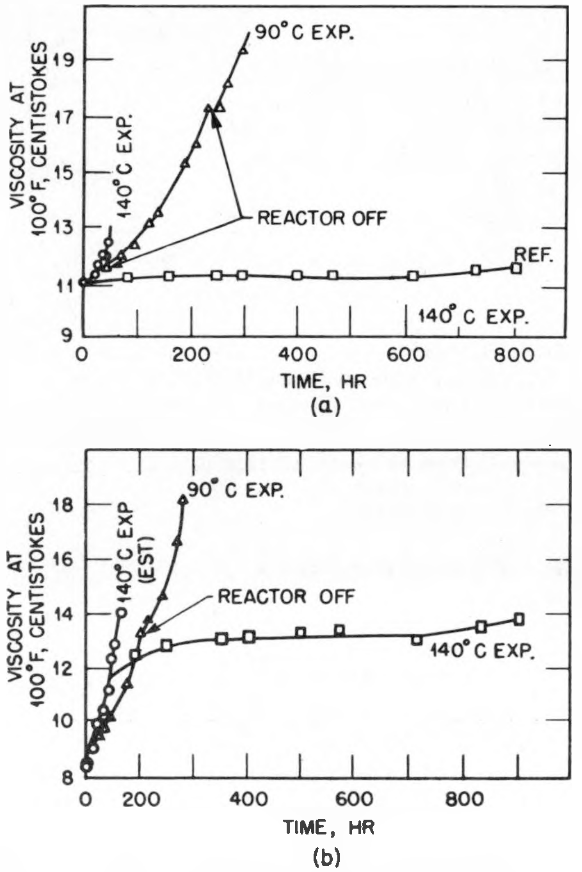


Fig. 1.1—Variation of viscosity at 100°F in accelerated oxidation tests with, and without, reactor radiations. (a) Octadecylbenzene: 5% didodecyl selenide and saturated with quinizarin (no quinizarin in 90°C reactor experiment). (b) Di(2-ethylhexyl) sebacate: 20% 1-methylnaphthalene (reference tests performed with iron and copper catalysts present).

2. Tests With and Without Reactor Radiations. Figure 1.1 shows typical data on these comparisons. The most striking observation about the experiments in the absence of reactor radiations was the sharp increase in viscosity at the beginning of the oxidation. This is shown in Fig. 1.1 and occurred only with those formulations containing 1-methylnaphthalene and/or iodobenzene, whose boiling points are 240 and 189°C, respectively. It seems likely that this effect was caused by evaporation and/or decomposition of these relatively low boiling materials in the early stages of the test.

Despite the initial viscosity increase in the reference experiments, the thickening effects due entirely to thermal oxidation are quite minor when compared with those which occur in the presence of reactor radiations. The same holds true for the formation of nonvolatile acids. Figure 1.2 illustrates the latter point graphically with a typical fluid, compounded di(2-ethylhexyl) sebacate. At first glance it seems unusual that the 140°C curve, as illustrated, shows less acid formation than the 90°C curve. However, at 140°C a larger percentage of total acids was volatilized. Thus, when total acidity is considered (total acidity was not available for the reference test), the situation is changed and the 140°C test yielded more acid than the 90°C experiment because of greater volatile-acid formation.

3. Tests at 80 to 90°C. Figure 1.3 presents the changes in 100°F viscosity and in acidity of the four oils subjected to in-pile oxidations

714 188

DECLASSIFIED

at 80 to 90°C.* The effect of the continuation of oxygen flow during periods of reactor shutdown is important. In Fig. 1.3 vertical displacements in the curves occur during such periods, and the slopes of the curves after these periods tend to decrease slightly. These vertical displacements are due to a combination of two factors: (1) degradation continued at a lesser rate in the absence of combined flux but in the presence of the existing gamma flux and (2) the oils were more easily oxidized after irradiation. Similar displacements, but in a horizontal direction, can be noted in Fig. 1.1, where viscosity is plotted vs. time.

The test with alkylbenzene (mol. wt. ≅250) is peculiar in that a viscosity index† improver-thickener was included in this sample. The low viscosity of the alkyl aromatic was increased by adding the improver-thickener. The viscosity results given in Table 1.3 show the effect of this additive.

The improver-thickener depolymerized as a result of bombardment with reactor radiations in the oxidation test (thermal-oxidation tests gave no obvious depolymerization). The effect of this is noted in Fig. 1.3, which shows a decrease in viscosity near the start of the test. It is very significant that the viscosity increase due to radiation damage was such that the oil received a dose of 0.5×10^{18} neutrons/cm^2 before the original viscosity value was regained. This supports the feasibility of the idea of making a "constant viscosity" fluid with the use of suitable base oils and polymers. The depolymerization shown in Fig. 1.3 is also illustrated by a decrease in viscosity index, as shown in Fig. 1.4.

In the test with the octadecylbenzene base oil, an additional 4 per cent of didodecyl selenide

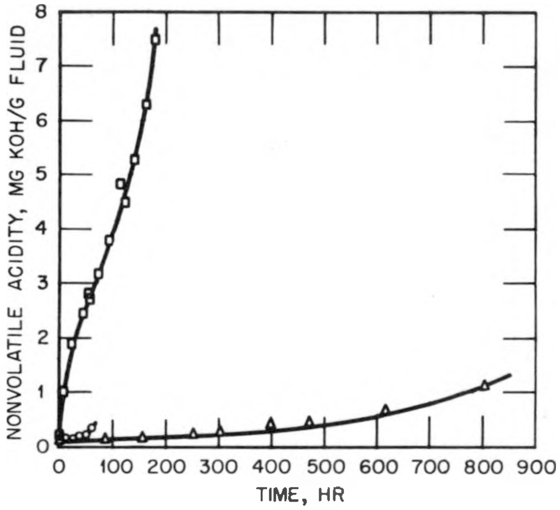


Fig. 1.2—Variation of nonvolatile acidity in accelerated oxidation tests with, and without, reactor radiations. Di(2-ethylhexyl) sebacate: 20% 1-methylnaphthalene, 5% didodecyl selenide, 2% iodobenzene; blend saturated with quinizarin. △, reference test at 140°C. ○, reactor test at 140°C. □, reactor test at 90°C.

Table 1.3—Effect of Adding V.I. Improver to Mixed Alkylbenzene (Mol. wt. ≅250)

	Viscosity in centistokes		
	At 100°F	At 210°F	V.I.
Alkylbenzene (mol. wt. ≅250) containing 2% didodecyl selenide	6.6	1.8	25
Alkylbenzene (mol. wt. ≅250) containing 2% didodecyl selenide and 4% poly(lauryl methacrylate)	14.1	3.8	185

---

*The radiation dosage is expressed as N = (thermal neutrons/cm^2) $\times 10^{-18}$.

†Viscosity index (V.I.), a term used by the petroleum industry, is related to the viscosity-temperature characteristics of an oil between 100 and 210°F. The original concept ascribed a V.I. of 100 to a Pennsylvania paraffinic oil and a V.I. of 0 to a less paraffinic Gulf Coast oil. Some extrapolations are permissible on either side of the 0 to 100 scale provided the fluids involved do not differ widely in viscosity.

189
DECLASSIFIED

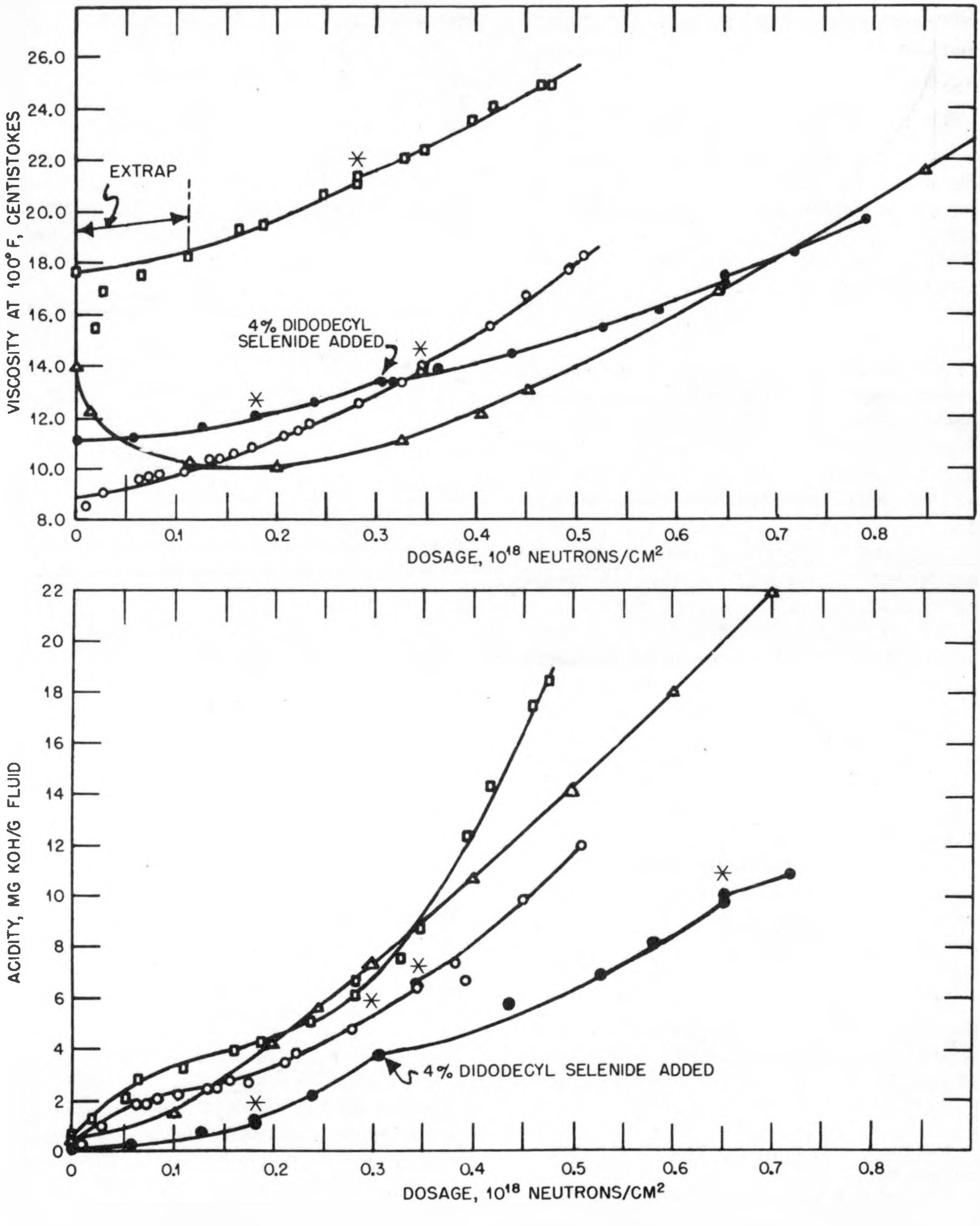


Fig. 1.3—Variations in acidity and viscosity at 100°F in reactor oxidation tests at 80 to 90°C. △, alkylbenzene (mol. wt. ≅ 250): 2% O-1, 4% S-14. ●, octadecylbenzene: 2% O-1, iron and copper wires. ○, di(2-ethylhexyl) sebacate: 5% O-1, 2% R-2, 20% S-1, S D-2. □, poly(propene oxide)-B: 5% O-1, 2% R-2, S D-2. ∗, reactor shutdown period. (See footnote to Table 2 for additive code.)

714 190

DECLASSIFIED

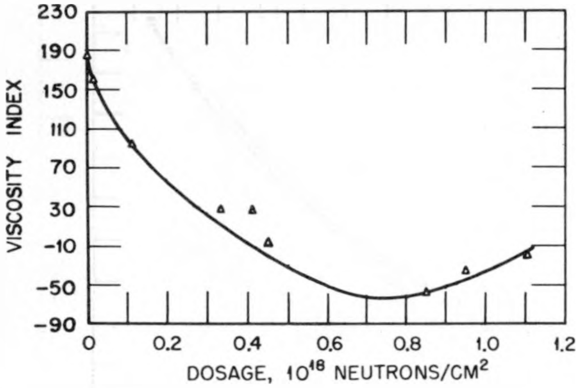


Fig. 1.4—Variation of viscosity index in reactor oxidation test at 80°C. Alkylbenzene (mol. wt. ≅ 250): 2% didodecyl selenide, 4% poly(lauryl methacrylate).

was added after the initial break in the viscosity-dosage curve. This had the effect of decreasing appreciably the slope of both the viscosity and the total-acid curves on continuation of the test.

In Fig. 1.3 the relative thickening of the four compounded oils can be pictured by comparing the percentage of viscosity increase at a specific dosage of N = 0.5. The octadecylbenzene is the best of these four with an increase of 36 per cent. The oxide polymer is next with 45 per cent, followed by the diester which exhibited an increase of 100 per cent over the original viscosity. The behavior of the viscosity index improved oil is difficult to compare on the same basis since the viscosity at N = 0.5 is the same as the starting viscosity. The curve passes through a minimum at N = 0.175, after which the controlling factor is the thickening, due to the action of radiations, of the base fluid. For a ΔN of 0.5 beyond the minimum, i.e., from N = 0.175 to N = 0.675, the viscosity increased from 10 to 17.6 centistokes at 100°F. This represents an increase of 76 per cent; this value may be considered with the percentages already cited for purposes of rough comparison.

Consideration of the acidity-dosage curves in these tests gives a slightly different story. The octadecylbenzene exhibited the least acid formation followed in order by the diester, viscosity index improved alkylbenzene, and poly(propene oxide). The last is seen to have given off three times the amount of acids evolved by the compounded octadecylbenzene. In comparing the two alkylbenzene derivatives, it is apparent that the less branched octadecylbenzene (mainly 2-phenyloctadecane) is superior to the mixed alkylbenzene (mol. wt. ≅250).

Of the catalysts used in the octadecylbenzene experiment, the iron was still bright while the copper had a black coating. The latter points to the need for a metal deactivator such as quinizarin.

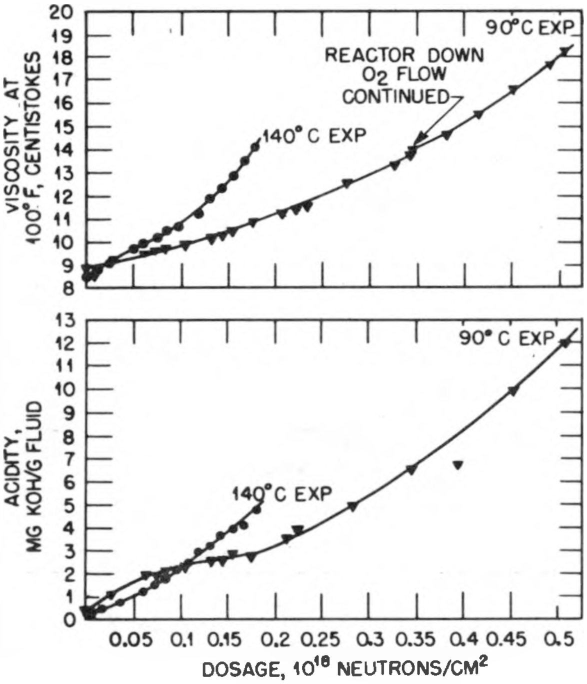


Fig. 1.5—Comparisons of viscosity and acidity variations in reactor oxidation tests at 90 and 140°C. Di-(2-ethylhexyl) sebacate: 5% didodecyl selenide, 2% iodobenzene, 20% 1-methylnaphthalene; blend saturated with quinizarin.

4. <u>Tests at 90 and 140°C</u>. Figure 1.5 depicts the viscosity increase at 100°F and the total-acid formation for a compounded di(2-ethylhexyl) sebacate oxidized at the two temperatures. For the 140°C oxidation, the sebacate oil exhibited a 100°F viscosity increase which is about twice that observed for the 90°C test. The acidity curves also follow this trend. The approximately doubled rate of deterioration is somewhat less than would be expected, strictly from the standpoint of a thermal process, from the

DECLASSIFIED

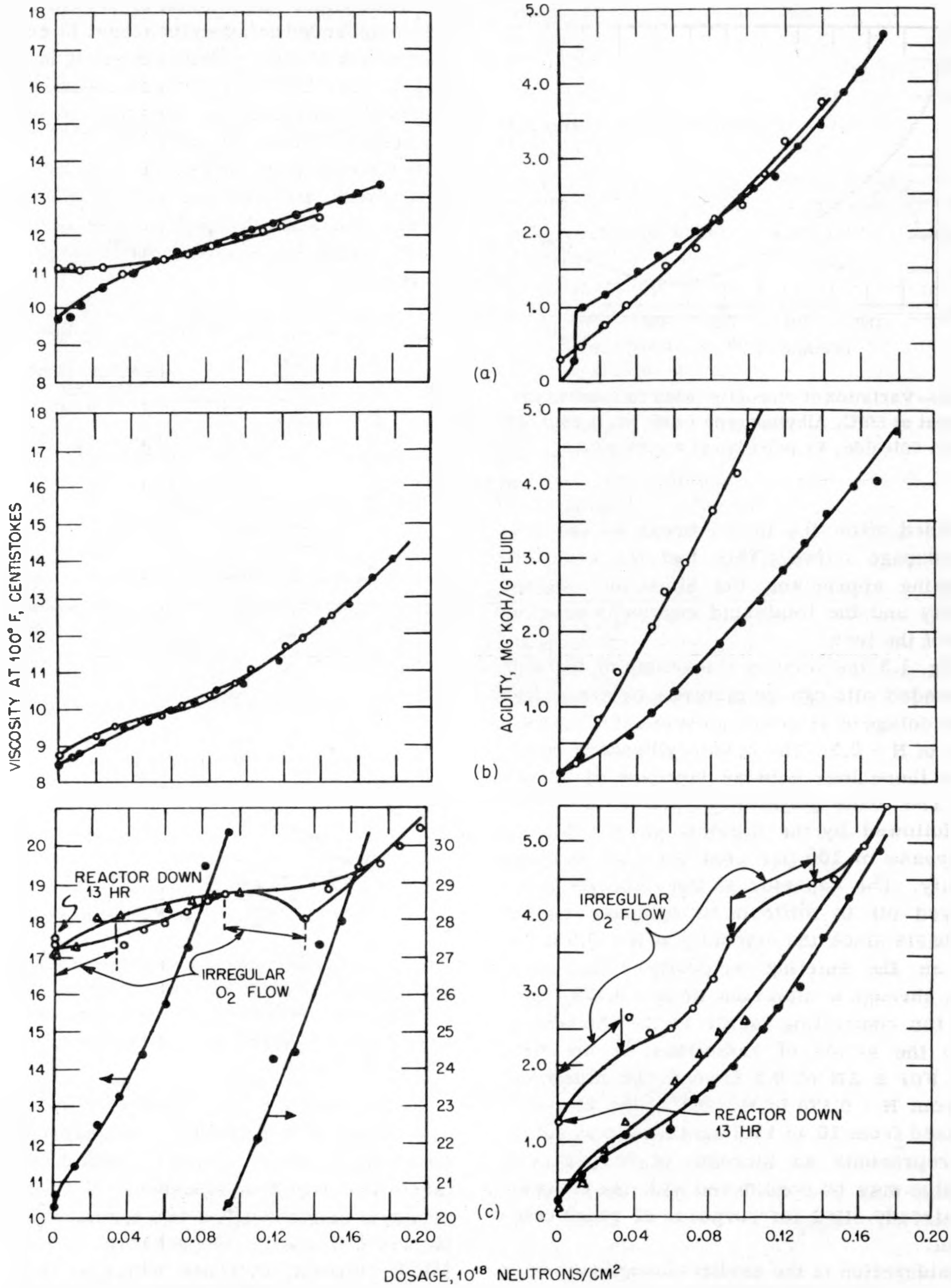


Fig. 1.6 — Comparisons of viscosity and acidity variations in reactor oxidation tests at 140°C. (a) Octadecylbenzene: 5% O-1, S D-2; ●, 6% R-2; ○, no R-2. (b) Di(2-ethylhexyl) sebacate: 5% O-1, S D-2, 20% O-1; ●, 2% R-2; ○, no R-2. (c) ●, solvent-refined western paraffinic lube oil (150N): 5% O-1, 6% R-2, S D-2, 20% S-1; △, *o*-poly(propene oxide)-B: 5% O-1, 2% R-2, S D-2. (See footnote to Table 7 for additive code.)

DECLASSIFIED

50°C increase in oxidation temperature. However, the change in rate seems within the variation expected from a photochemical process.

5. Tests at 140°C. Figure 1.6 summarizes the data obtained for viscosity increase and acidity in the six tests at this temperature. The compounded octadecylbenzene oil, either with or without iodobenzene, is the best of the fluids, both from the viscosity increase and the acidity standpoints. Apparently iodobenzene was ineffective in decreasing the rate of deterioration of the octadecylbenzene fluid in this test. It is likely that iodobenzene, which boils at 189°C, volatilizes off and/or decomposes into volatile products in a short time at this temperature. Again, with the compounded di(2-ethylhexyl) sebacate oil, the presence of iodobenzene did not reduce the rate of viscosity increase, although its presence effected a reduction of 50 per cent in the amount of acids formed. The loss of fluid in these tests is undoubtedly of some importance. However, in all the reactor experiments where much mechanical handling was necessary, it was impractical to measure these losses.

The poly(propene oxide)-B tests are not conclusive because of the operational difficulties which caused plugging of the exit lines. In these tests it can be noted that very little viscosity increase occurred up to a dose of $N = 0.14$. However, the rate of increase after this point was greater than that observed for any of the oils oxidized at this temperature except for the mineral oil. The latter was the worst oil in this respect. The mineral oil even with near maximum compounding is thus demonstrated to be unsuited for application in the presence of reactor flux and excess oxygen.

Thermal Oxidation of Irradiated Fluids

Figure 1.7 summarizes the data on the oxidation work conducted in Zeitfuchs viscometers with small samples of irradiated oils. These oils had been exposed in vented ampoules for four weeks in the X-10 reactor. Unirradiated fluids were oxidized in the same manner for comparison with the irradiated materials. In all cases the irradiated oils thickened much more rapidly than the original fluids. This difference ranged from negligible for the amylbiphenyl to a great amount for the sebacate in the following increasing order: amylbiphenyl < paraffinic mineral oil < sulfur-linked polyether < aliphatic diester. The following two reactions probably were occurring in this test:

1. Accelerated distillation of volatile matter formed in the reactor and still in solution
2. Oxidation of more reactive materials formed in the reactor

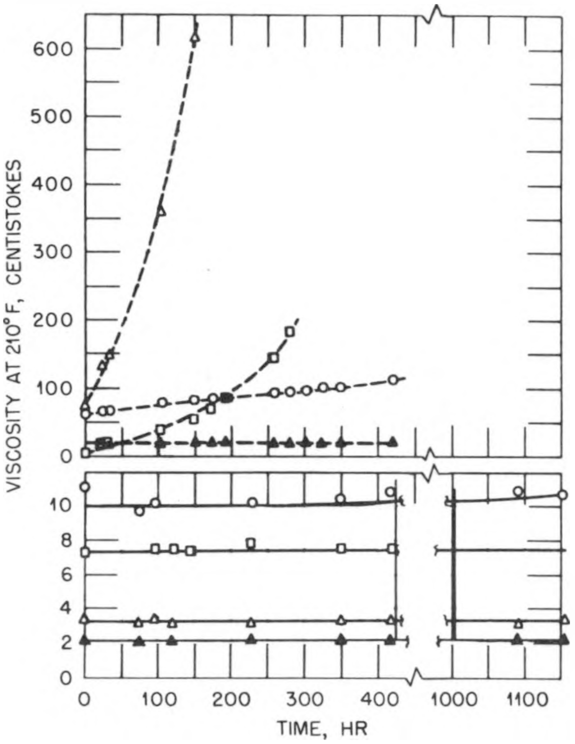


Fig. 1.7—Special oxidation tests in Zeitfuchs viscometer. Viscosity variations of original and irradiated oils. ---, original oil. ——, oil irradiated for four weeks at 75% maximum X-10 reactor flux. △, di(2-ethylhexyl) sebacate with 2% didodecyl selenide. □, 16,19-dioxa-13,22-dithitetratriacontane. ○, solvent-refined western paraffinic lube oil (SAE 30). ▲, amylbiphenyl with 2% didodecyl selenide. Test conditions: 210°F, excess oxygen, and no catalysts.

Poly(propene oxide) fluids showed small changes in viscosity until the samples were blown with nitrogen. Much larger differences then became apparent as volatile matter was removed. Such large volume losses were encountered that the experiments with this base oil could not be completed because insufficient liquid remained to conduct viscosity determinations. This is directionally the same as was noted with the sulfur-linked polyether. The extremely high rate of thickening of the sebacate on oxidation after irradiation is further indication of the radiation instability of this base oil alone or lightly inhibited.

Conclusions

1. Increases in the viscosity and acidity of fluids in accelerated thermal-oxidation tests outside the reactor are minor when compared with these same changes which occur in the presence of reactor radiations.
2. In oxidation tests in the reactor the rate of fluid damage is much less during reactor down periods. However, oils are more susceptible to thermal oxidation after irradiation than before, although individual oils vary widely in this respect.
3. Alkyl aromatic compounds are the most promising of the compounded base oils tested. The aliphatic diesters are next in order, with the oxide polymers third, and mineral oils a poor last.
4. Highly branched chain structures appear to be oxidized more rapidly in the reactor than less branched materials.
5. The most promising oxidation inhibitors for general use with the types of base oils studied are organic compounds containing sulfur or selenium. When injected during an oxidation run, a selenide inhibitor showed a positive effect in the reactor by causing a decrease in the rate of deterioration.
6. Viscosity index improver-thickeners, such as poly(lauryl methacrylate), depolymerize in reactor oxidation tests. As a result of this, one oil was found to possess the same viscosity at 100°F after a dose of 0.5×10^{18} thermal neutrons/cm^2 as at the start of the oxidation.

REFERENCES

1. C. B. Ellis, Reactor Sci. Technol., Vol. 1, 2: 63 (1951).
2. Committee D-2 Report, ASTM Standards 1949, Part 5, p. 1110 (1950).
3. E. H. Zeitfuchs, Oil Gas J., 44: 99 (1946).
4. D. M. Richardson, Calorimetric Measurement of the Radiation Energy Dissipated by Various Materials Placed in the Oak Ridge Pile, Report ORNL-129, p. 26, Oct. 1, 1948.
5. M. Goldberger, J. Stephenson, and A: M. Weinberg, Neutron Flux in W Lattice, Report CP-2439, Nov. 30, 1944.
6. Private communication from V. P. Calkins of the Fairchild-NEPA Project.

PART II. BEARING-LUBRICATION TESTS

ABSTRACT

These tests were conducted to investigate the effect, in open systems, of reactor radiations on the lubrication process and on lubricants operating in standard bearings, bushings, and gears. Lubricants from three basic types of synthetic oils were employed in experiments designed to demonstrate the feasibility of using such materials in functional equipment. The base oils and additives had been demonstrated to be superior in static irradiations and oxidation tests in the X-10 reactor. Three units in which ball bearings were driven with air turbines were operated in the reactor for 300 hr at 10,000 rpm and 140°C. Three motor-driven units in which ball bearings, journal bearings, and gears were used were also operated in the reactor for 100 hr at 80 rpm and 140°C. Each of the six in-pile tests was duplicated in the absence of radiations to obtain reference results. Data on mechanical changes in the operating parts and on deterioration of the lubricants are presented and discussed.

Table 2.1 identifies the oils employed in these tests. Two in-pile experiments were performed with each of the lubricants, one in a low-speed and one in a high-speed unit.

Low-speed Bearing lubrication Tests

These tests were conducted primarily to determine the effect of reactor radiations on the

114 194

DECLASSIFIED

Table 2.1—Lubricants Employed in Bearing-lubrication Tests

Base oil	Additives, wt. %
Di(2-ethylhexyl) sebacate	20% 1-methylnaphthalene, 5% didodecyl selenide, 2% iodobenzene; blend saturated with quinizarin
Poly(propene oxide)-B (one ether and one ester end group)	5% didodecyl selenide, 2% iodobenzene; blend saturated with quinizarin
Octadecylbenzene	5% didodecyl selenide, 6% iodobenzene; blend saturated with quinizarin

lubrication process. Loaded journal bearings and gears were operated in the X-10 reactor, and torque and friction measurements during reactor operating periods and down periods were obtained along with final-wear results. Comparative data were then secured on reference tests outside the reactor.

1. Description of Apparatus. The apparatus was driven by a 27-volt 10,000-rpm permanent magnet d-c motor which powered test specimens operating in a bath of lubricant. The motor was mounted vertically and was supported on two metal balls so that it rotated freely as a unit. Power was transmitted through a gear-reduction unit to a journal which was loaded by applying air pressure to the split journal bearings. This load was applied by means of a "nut cracker" from a bellows actuated by external air pressure. The torque generated by the load applied to these bearing halves caused the motor to pivot on its supporting balls. This rotation was balanced by air pressure which flowed through a small orifice and impinged on a torque arm mounted on the motor body. The air pressure required to keep this torque arm "floating" on an electrical contact provided direct measurement of the motor torque.

The output speed of the motor was reduced through the gear train in the ratio of 71 to 1. Constant output speed was maintained at approximately 80 rpm by controlling the input voltage. Speed was determined by impulses which resulted from the passage of the commutator segments over the brushes. These impulses were transmitted by a thermocouple wire to an oscillograph.

Figure 2.1 shows the parts of the test assembly. Figure 2.2 shows the gears, shaft, and bearing components of a test unit. The journal and journal bearings were standard wear parts taken from the Almen Wear Test machine.* The standard ball bearings were of approximately 3.5 to 5 mm bore. In all the tests the parts shown in Fig. 2.2 were weighed prior to operation of the unit and were reweighed at the completion of the test to yield wear data in terms of weight change.

2. Test Procedure. Three of these assemblies, each containing 50 ml of a different lubricant, were operated in hole 54N of the X-10 reactor. It was planned to run the three units for a 100-hr period in the reactor in order to obtain direct comparisons among the three oils, as well as direct comparisons for each oil with and without reactor radiations. Only one of the three rigs operated for the entire period, which was actually 105 hr. This was the poly(propene oxide)-B unit. The di(2-ethylhexyl) sebacate and octadecylbenzene units operated for only 95 and 55 hr, respectively, because of motor commutator failures.

Temperature was maintained at 140°C by controlling the voltage input to the heaters. Continuous torque readings were taken at appropriate intervals and close supervision was maintained during reactor down periods so that any abrupt changes would be noticed as they occurred. Load conditions were carefully controlled by adjustment of the air pressure to the load-actuating bellows. Reference runs were conducted in which the operating conditions were identical with those of the reactor runs except

---

*This machine was designed by J. O. Almen and manufactured by General Motors. It is widely used but is no longer available.

DECLASSIFIED

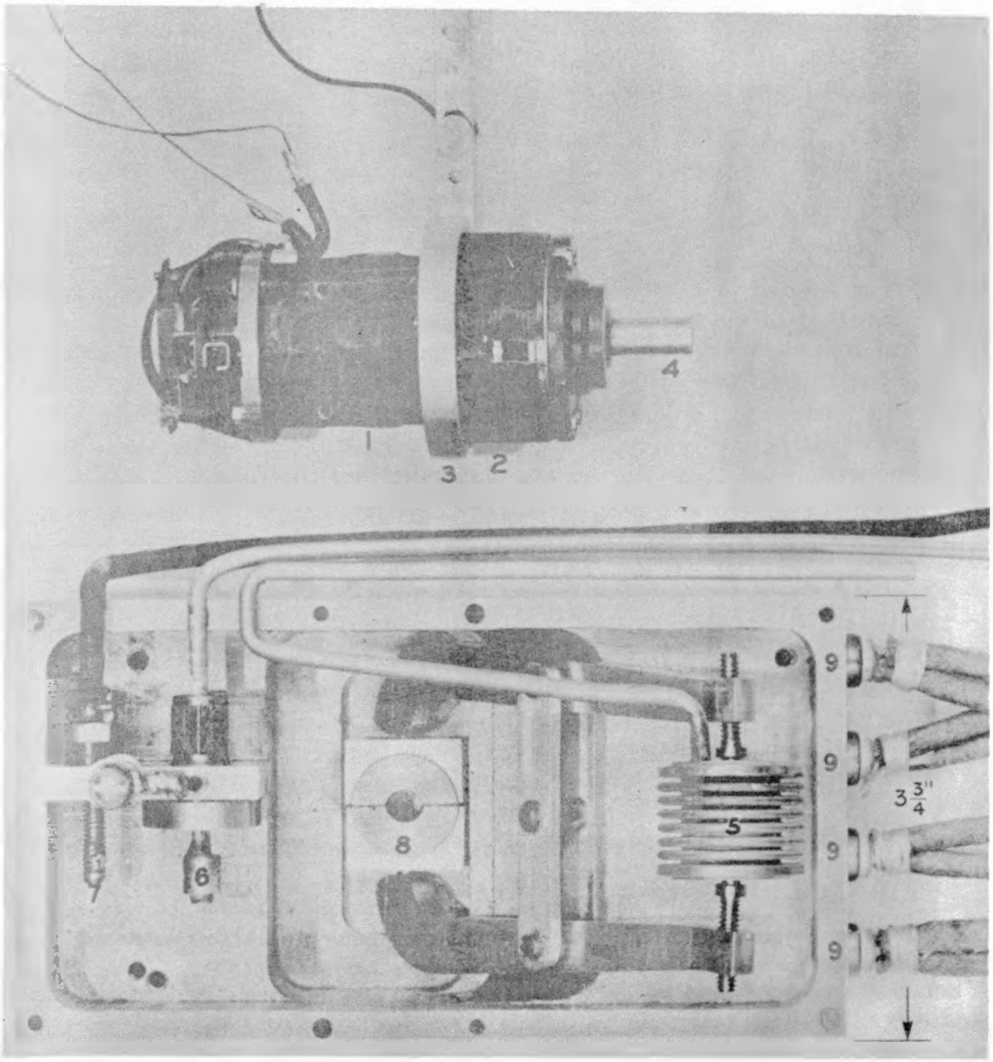


Fig. 2.1—**Low-speed bearing test unit.**

1. 27-volt 10,000-rpm d-c drive motor
2. Reduction gear box, to 145 rpm
3. Torque arm
4. Bronze output shaft
5. Bellows loading device
6. Orifice for torque measurement
7. Hot lead to motor
8. Steel bushings
9. Leads to heater

714 196

DECLASSIFIED

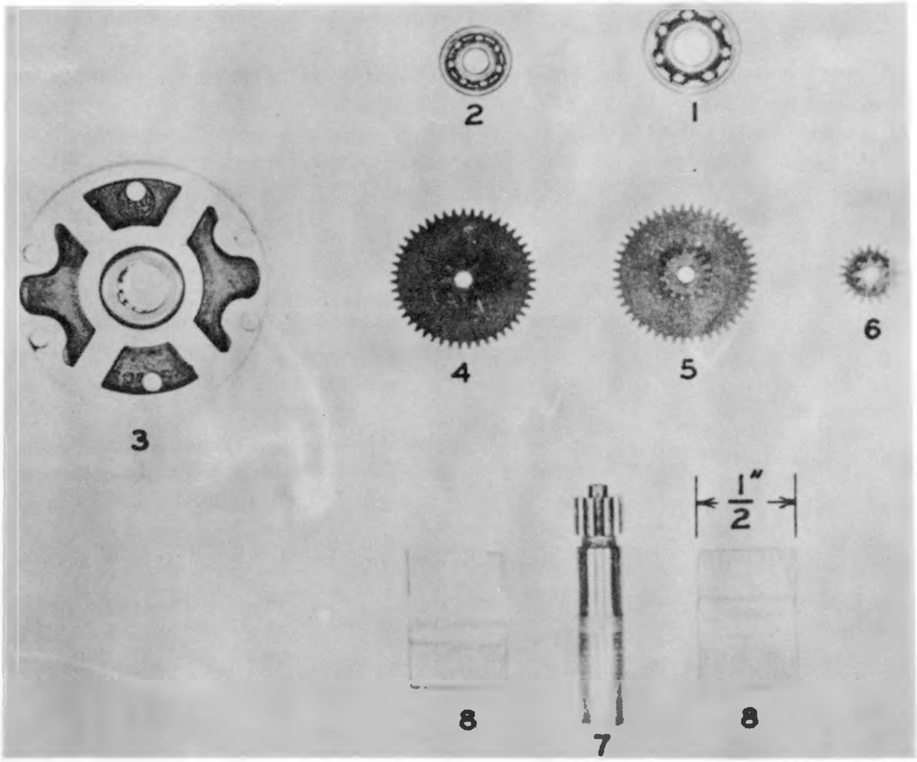


Fig. 2.2—Weighed parts of low-speed bearing test unit.

1. Lower armature support bearing, 5-mm bore
2. Upper armature support bearing, 3.5-mm bore
3. End bell and needle bearing
4,5,6. Reduction gearing
7. Bronze shaft (Almen machine specimen) and drive spline
8. Steel bushings (Almen machine specimen)

for the presence of reactor radiations. Thus data from the reference and reactor runs are directly comparable.

3. Results. (a) Torque Data. Figure 2.3 is a summary of the torque data obtained in the reference and reactor runs. Motor torque in the latter was significantly higher than in the former. In the case of the poly(propene oxide)-B oil, this statement holds true only initially since the torque of the reactor test decreased below that of the reference run at about the one-third point. This result and the wear data to be described signify that this oil actually improved in lubricity on irradiation. However, initially the motor torque for the poly(propene oxide)-B oil was at a high level. The torque data from these tests are evidence that the lubrication process was adversely affected by reactor radiations and/or the fluids became poorer lubricants in the reactor.

There was a reactor shutdown period (68.9 to 69.9 hr) while the units containing sebacate and polymer were operating. At this time the motor torque was observed as the neutron flux was abruptly stopped. No change in any of the operating characteristics of the two units occurred during this period, indicating that no sudden change in the lubrication process took place. Instead, more gradual changes are indicated by the comparison of the torque curves for the reference and the reactor runs. These variations are more indicative of changes taking place in the lubricant during irradiation than of changes in the lubrication process itself. How-

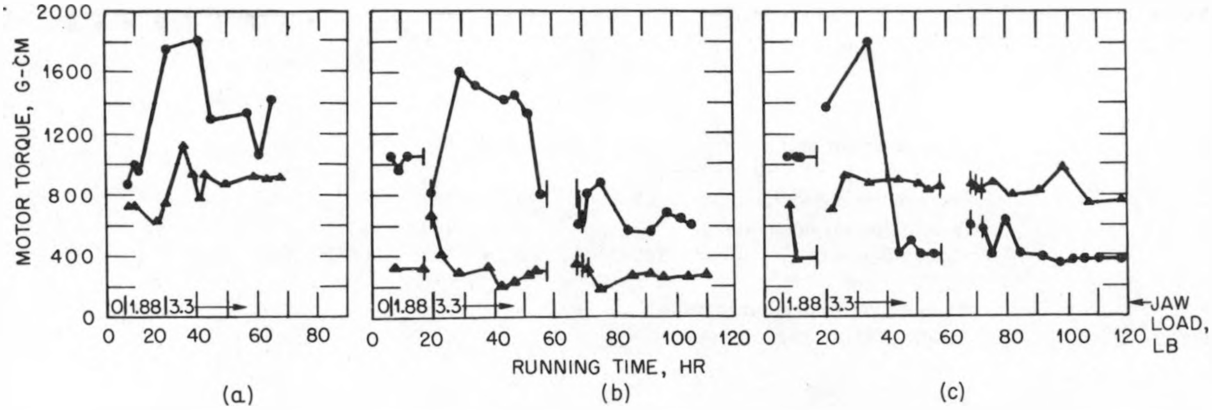


Fig. 2.3— Low-speed bearing lubrication tests. Comparison of motor torque with, and without, reactor radiations. (a) Octadecylbenzene with 5% O-1, 6% R-2; S D-2. (b) Di(2-ethylhexyl) sebacate with 5% O-1, 2% R-2, 20% S-1; S D-2. (c) Poly(propene oxide)-B with 5% O-1, 2% R-2; S D-2. (See footnote to Table 7 for additive code.) -●-●-, test in hole 54, X-10 reactor. -▲-▲-, reference test (without radiation); 1-lb jaw load = 1200 psi. ||, motor not running.

ever, the data do not exclude the latter possibility; they merely make it appear less likely.

Examination of the motors from the reactor tests showed that thick lacquer coatings had been built up on the commutators. The lacquer deposits were also present on the carbon brushes and apparently acted as insulators which, in the case of the sebacate and octadecylbenzene units, unduly increased electrical resistance.

(b) Wear Data. In bearing-lubrication tests of this type, wear data expressed as weight loss of the moving parts are sometimes more significant than torque data in evaluating the lubricant. This follows from the fact that high torque does not necessarily mean high wear, although high wear usually is accompanied by high torque. In both the reference and in-pile tests it was observed that weight changes were insignificant except for the steel bushings and the bronze shafts, the latter losing as much as 1 per cent of the original weight. In the reference runs the parts lubricated with the di(2-ethylhexyl) sebacate and octadecylbenzene oils showed about the same weight loss, whereas the parts lubricated with the oxide polymer showed markedly higher loss. This is shown in Table 2.2 where the data are summarized. This order was reversed in the reactor runs, and the oxide polymer unit showed not only significantly lower weight loss than in the reference test but also exhibited the lowest loss of the three reactor units. In the reactor tests the relation between the weight losses for the poly(propene oxide)-B, di(2-ethylhexyl) sebacate, and octadecylbenzene oils is 1 : 3.1 : 4.5, respectively. The wear data and the torque data both signify that the poly(propene oxide)-B improves as a lubricant on irradiation. For the other two oils the reactor condition was the more severe.

For the in-pile tests the torque and the wear data are in agreement; the oxide polymer, sebacate, and the octadecylbenzene rank in that order by either criterion. In the reference tests torque data rate the sebacate first and the other two oils about equal. The only discrepancy in the correlation is the low value for wear with the octadecylbenzene in the reference tests. In any event the oxide polymer is the first choice for a lubricant under the test conditions in a radiation atmosphere.

Falex wear tests tend to corroborate the improvement in wear properties of the poly(propene oxide) type of oil on irradiation. In this work a sample of uncompounded poly(propene oxide) (one ether and one hydroxyl end group) was irradiated in the X-10 reactor for an integrated dose of 1.6×10^{18} thermal neutrons/cm^2. The final product was partially distilled for another purpose, and the recombined material

DECLASSIFIED

Table 2.2 — Summary of Wear and Torque Data in Low-speed Bearing Tests

	Total wear, mg		Torque, g-cm			
			Reactor		Reference	
Base oil in unit	Reactor	Reference	Max.	Min.	Max.	Min.
Poly(propene oxide)-B	22	70	1800	400*	1000†	400
Di(2-ethylhexyl) sebacate	68	8	1600	550	700	200
Octadecylbenzene	100	9	1800	900	1100	600

*Lower value predominant.
†Higher value predominant.

was used for the wear tests. Comparison was made with original oils which had, and which had not, been similarly distilled. Table 2.3 summarizes the conditions of the tests and the data obtained in experiments on the Falex Lubricant Tester.*

In the Falex extreme-pressure test the film strength or antiseizure value of a lubricant is measured. A ¼-in. shaft rotates in a pair of steel V blocks. Load is gradually applied until the oil film ruptures and a metal-to-metal contact occurs. This point is considered as failure. Irradiated poly(propene oxide) showed appreciably improved film strength in this test.

The Falex wear test also utilizes a ¼-in. shaft turning in a pair of steel V blocks. A relatively low weight loss of the shaft is the index of good antiwear properties in the lubricant. The wear properties of irradiated poly(propene oxide) actually improved somewhat over the unirradiated product in this test.

Additional wear tests on the Four-ball Machine† were erratic but did indicate that irradiation of the poly(propene oxide) did not impair its wear properties in room-temperature tests.

(c) Effect on the Oil. Although the primary purpose of the low-speed bearing tests was to observe the effect of reactor radiations on the lubrication process, the damage to the lubricant, since it contributes to this effect, is also of interest. Table 2.4 summarizes the data on the thickening of the three oils in the experiments. In the reference runs the three fluids showed significant viscosity increases; however, these are minor when compared to the thickening experienced in the reactor. The viscosity increases in the reactor tests were quite high, considering the low dosage. This may be an indication that thickening was catalyzed by the action of the metals despite the presence of the quinizarin. In the reactor tests the viscosity at 100°F for the poly(propene oxide)-B increased 75 per cent, octadecylbenzene increased slightly more with 81 per cent, and the sebacate oil thickened the greatest amount with 262 per cent. In the reference tests thickening was considerably less but still significant. The 100°F viscosity increase was about 16 per cent for both the polymer and the octadecylbenzene and was 41 per cent for the diester. Thus even the reference exposure in the presence of metal catalysts at 140°C had an appreciable effect.

Conclusions

On the basis of these limited tests under the conditions described, the following conclusions can be drawn:

1. High-speed antifriction and low-speed journal bearings operated in the X-10 reactor with lubricants based on poly(propene oxide)-B (one ether and one ester end group), di(2-ethylhexyl) sebacate, and octadecylbenzene. A temperature of 140°C, fluxes of 0.5 to 0.8 × 10^{12} neutrons/cm^2/sec, and dosages of 0.4 to 0.6 × 10^{18} neutrons/cm^2 were employed. None of the bearings was run to mechanical failure at the

---

*The Falex Lubricant Tester is manufactured and described by the Faville Levalley Corp., Chicago.

†The Four-ball Machine is manufactured and described by the Precision Scientific Co., Chicago.

714 199

Table 2.3 — Effect of Irradiation on the Wear Properties of Poly(propene oxide)

Test	Original oil	Distilled oil*	Irradiated and distilled oil†
Load at failure, lb (Falex extreme-pressure test: load applied at rate of 250 lb/min; steel on steel; 19.6 fpm; room temp.)	1250	1250	2250
Weight loss of steel shaft, mg (Falex wear test: 500-lb jaw load; 30-min test at 19.6 fpm; room temp.; steel on steel)	10.8	13.3	3.5

*Distilled at 1 μ, and 5 per cent distillate remixed with 95 per cent residue.

†Irradiated in X-10 reactor at 30°C and 75 per cent maximum flux to N = 1.61. Distilled at 1 μ, and 20 per cent distillate remixed with 80 per cent residue.

Table 2.4 — Lubricant Deterioration in Operating Bearing Tests in the X-10 Reactor
[Test conditions: Temperature, 140°C. Neutron dosage: N(low speed) = 0.38; N(high speed) = 0.60; refers to total dosage, not merely to dosage received during operation. Flux: low-speed tests, 87% of maximum; high-speed tests, 50% of maximum. Time in reactor: low-speed units, 132 hr; high-speed units, 399 hr.]

	Viscosity at 100°F, centistokes					Viscosity at 210°F, centistokes				
		Low speed		High speed			Low speed		High speed	
Oil identity*	Original	Ref.	Reactor	Ref.	Reactor	Original	Ref.	Reactor	Ref.	Reactor
Di(2-ethylhexyl) sebacate; 5%	8.8	13.0	32.8	13.3	58.0	2.5	3.5	6.5	3.6	8.8
O-1, 2% R-2, 20% S-1, S D-2	8.8			11.4		2.5			3.1	
Poly(propene oxide)-B; 5% O-1,	17.7	20.5	31.0	19.5	40.3	4.3	4.8	6.1	4.6	6.4
2% R-2, S D-2	17.7			19.6	33.9	4.3			4.6	5.8
Octadecylbenzene; 5% O-1, 6%	9.8	11.4	17.7	11.6	34.3	2.7	2.9	3.9	2.8	5.9
R-2, S D-2	9.8			11.3		2.7			2.8	

*Additive code: O-1, didodecyl selenide; R-2, iodobenzene; S-1, 1-methylnaphthalene; D-2, quinizarin (S for saturated, ~0.2 per cent of maximum).

operating temperature; therefore these dosages do not indicate the limit of operability.

2. The lubrication process does not appear to change with the sudden removal of neutron flux as in reactor shutdown.

3. The presence of reactor radiations markedly shortens the useful life of a fluid functioning as the lubricant: (a) in lightly loaded high-speed ball bearings and (b) moderately loaded journal bearings. Compared to lubricant damage in the presence of reactor radiations, that suffered in the absence of radiations under identical conditions is minor.

4. The useful life of bearings is considerably shortened when operating in the presence of reactor radiations. This is attributed to lubricant failure rather than mechanical failure.

5. In the absence of radiations the compounded di(2-ethylhexyl) sebacate oil is the best lubricant of those tested, followed by the poly(propene oxide)-B and octadecylbenzene fluids which are about equivalent.

6. The compounded sebacate is a better lubricant than the octadecylbenzene in the presence of reactor radiations, even though this fluid undergoes greater deterioration.

7. Wear data from bench tests on irradiated poly(propene oxide) (one ether and one hydroxyl end group) tend to confirm the results of the functional tests, which indicate that the wear properties of this type of oil actually improve upon irradiation.

8. The compounded poly(propene oxide)-B is the most satisfactory lubricant in a reactor atmosphere. This is based on wear and torque data, appearance of the lubricated parts, and oil deterioration.

REFERENCE

1. Committee E-1 Report, ASTM Standards 1949, Part 1, p. 1261 (1950).

October 1951

A SURVEY OF HOMOGENEOUS-REACTOR CHEMICAL PROCESSING

By F. R. BRUCE

Oak Ridge National Laboratory

Report ORNL-1136 (Rev. 2)

ABSTRACT

The chemical processing, involving the least number of unknowns, for treating a homogeneous plutonium producer would consist in the following steps: 18-day decay of neptunium to plutonium, evaporation of the uranyl sulfate fuel to recover heavy water, conversion to a light water system, and, finally, separation of uranium, plutonium, and fission products by two tributyl phosphate extraction cycles. Uranium and plutonium losses would be about 0.2 per cent over-all. Using this scheme, 1550 kg of uranium are processed per day per kilogram of plutonium produced. From a long-range standpoint a more attractive process consists in coupling continuous plutonium removal by ion exchange to uranium decontamination by tributyl phosphate extraction. This scheme permits operation of the reactor at a higher fuel burn-up, and only 600 kg of uranium per day are processed per kilogram of plutonium produced.

The U^{233}-breeder processing which seems most assured of success consists in evaporation of the thorium oxide blanket to dryness for heavy water recovery, dissolution of the thorium oxide, and U^{233} recovery by methyl isobutyl ketone extraction. The thorium would be separated from fission products by tributyl phosphate extraction. Uranium and thorium losses would be about 0.1 per cent. The core material would be processed by tributyl phosphate extraction.

The major uncertainties involved in the processing of homogeneous reactors include radiation stability, the handling of heavy water and $N^{15}O_3^-$ ion, the chemical state of plutonium formed in the reactor, the solvent-extraction behavior of short-cooled material, the chemistry of neptunium, and the chemistry of bentonite. Reasonably definitive answers to these problems should be obtained in the near future in order that the optimum chemical process for a homogeneous plutonium producer may be tested on the Homogeneous Reactor Experiment shortly after start-up.

DECLASSIFIED

INTRODUCTION

Chemical processing attendant to the operation of nuclear reactors has three primary objectives: (1) isolation of the product, (2) removal of fission-product poisons, and (3) reclamation of the fuel or source material. The frequency of chemical processing in the case of a plutonium producer is determined by three factors. [redacted] The second factor determining the processing cycle is the rate of depletion of the reactor fuel, since, on reaching a limiting composition with respect to the fissionable isotope, the fuel must be replenished by either reenrichment or the addition of highly enriched material. The third factor is the rate of build-up of fission-product poisons, which lower the neutron economy. In a solid-fuel reactor the Pu^{240} build-up limits the time a reactor may be operated without chemical processing, and it is apparent that plutonium recovery requires solution of the metal, stringent chemical processing to permit reenrichment of the fuel, and, finally, refabrication of the fuel. Opposed to this, plutonium and fission products conceivably may be removed continuously from a solution reactor, and the machine may be operated until depletion of the fuel makes reenrichment necessary. Thus it is presumed that plutonium may be produced in homogeneous reactors with less frequent processing of the bulk source material and by an inherently simpler procedure consisting in fewer steps.

This article has two objectives. The first is to discuss the chemical processing of homogeneous reactors which may be operated for plutonium production or U^{233} breeding, employing, where possible, well-established processing techniques. The second objective is to outline processing approaches which may ultimately become important factors in establishing homogeneous reactors as the most economical means of producing plutonium and U^{233}.

PRESENT STATUS OF HOMOGENEOUS-REACTOR CHEMICAL PROCESSING

This section will discuss the chemical processing that would be recommended for recovering plutonium and for breeding U^{233} in the event that the decision was made to build forthwith a homogeneous reactor to accomplish either of these objectives. The reactor systems upon which this discussion is based are those described by the long-range planning group in Report ORNL-855, A Preliminary Survey of Large Scale Homogeneous Reactors. More recent developments in the homogeneous-reactor field are contained in Report ORNL-1096, Comparative Study of Feasibility and Economy of Homogeneous Reactors and Large Scale Reactors Producing Uranium-233.

Frequency of Chemical Processing for an Aqueous Homogeneous Plutonium Producer

The plutonium producer for which chemical processing cycles are to be outlined is based on the following design criteria:

Heat output	10^6 kw
Fuel composition	D_2O solution of UO_2SO_4
Fuel uranium concentration	92 g/liter
pH of fuel	2.0
Plutonium production	965 g/day
U^{235} consumed	1185 g/day
Isotopic % of U^{235} in feed	0.80
Isotopic % of U^{235} in waste	0.746
Moderator	D_2O
Molecular ratio D_2O/U	110
Weight of D_2O in core	175 metric tons
Weight of uranium in core	18.6 metric tons
Volume of core	2.05×10^5 liters
Plutonium concentration at 400 gross tons	0.037 g/liter

There are three schemes of operation possible for this reactor: (1) the reactor can be charged and discharged in one batch, (2) the reactor can be charged and discharged continuously, and (3) plutonium and high-cross-section fission products can be removed continuously from the reactor, with only a small amount of uranium removed each day for reenrichment. The frequency of the chemical processing of the reactor fuel for the first two schemes is determined by the amount of Pu^{240} which is allowable in the

DECLASSIFIED

final product.

Thus, of the three processing possibilities, continuous removal of plutonium and fission products, coupled with batchwise decontamination of the uranium, proves to be the most economical. This scheme possesses the added advantages of making possible the production of material of very low Pu^{240} content at only slight incremental cost and of contributing to safer reactor operation by decreasing the quantity of long-lived fission products in the reactor.

Batch Processing of a Plutonium Producer

After charging, the reactor would produce plutonium at the rate of 965 g/day, until a plutonium concentration of 600 g/ton was reached after about 12 days of operation. At this time the fuel would be withdrawn and chemically processed for plutonium removal and for uranium decontamination prior to isotopic enrichment. Since the fuel solution contains appreciable Np^{239}, approximately 18 days of cooling would be necessary to decrease the neptunium-plutonium ratio to 0.001.

The first step in the chemical processing would consist in removing heavy water from the uranyl sulfate in order that subsequent chemical processing might be conducted in a light water medium. The alternate procedure of accomplishing the separation of uranium, plutonium, and fission products in a deuterated system is less desirable. If solvent extraction is used, deuterated nitric acid would be required as a process reagent, and, furthermore, the solvent extraction of uranium by tributyl phosphate would result in the loss of a significant amount of deuterium as deuterated nitric acid and water of hydration.

The problem of dehydrating uranyl sulfate has not been investigated extensively on the Project, and the open literature on the subject is ambiguous. Uranyl sulfate forms mono-, di-, and trihydrates.[1] The monohydrate results from heating the trihydrate to 100°C, and at 300°C appreciable quantities of uranium trioxide are formed.

From this it appears that the separation of heavy water from uranyl sulfate would require calcination at 300°C. Special equipment would be necessary to accomplish this dehydration in the presence of fission products, and the operation would require considerable engineering research to assure its satisfactory operation.

In 1945 an evaporation step for separating heavy water from a uranyl carbonate–sodium carbonate solution was pilot-planted at this laboratory. In this work[2] a pot evaporator was employed to dehydrate the fuel at 130°C. With drying times of about 5 hr, heavy water recoveries of 99.9 per cent were obtained, and the heavy water was decontaminated from fission products by a factor of 10^2 to 10^3. These results strongly support the contention that heavy water systems may ultimately be handled satisfactorily.

After obtaining the uranium, plutonium, and fission products in a light water solution, the uranium and plutonium would be selectively extracted from the fission products with 30 per cent tributyl phosphate in a hydrocarbon diluent employing 6M to 7M nitric acid as a salting agent. Fission products would be scrubbed from the uranium–plutonium-bearing solvent with 3M nitric acid, and the solvent would be passed to a second column where plutonium would be removed by an aqueous solution of 0.03M ferrous sulfamate. The uranium would finally be stripped from the solvent with water in a third

UNCLASSIFIED

column. Both the uranium and plutonium streams would then be processed through another solvent-extraction cycle for final separation from fission products. After isotopic enrichment the uranium would be converted to uranium trioxide and reacted with deuterated sulfuric acid to form fuel solution. A schematic flow sheet of this is shown in Figs. 1, 2, and 3.

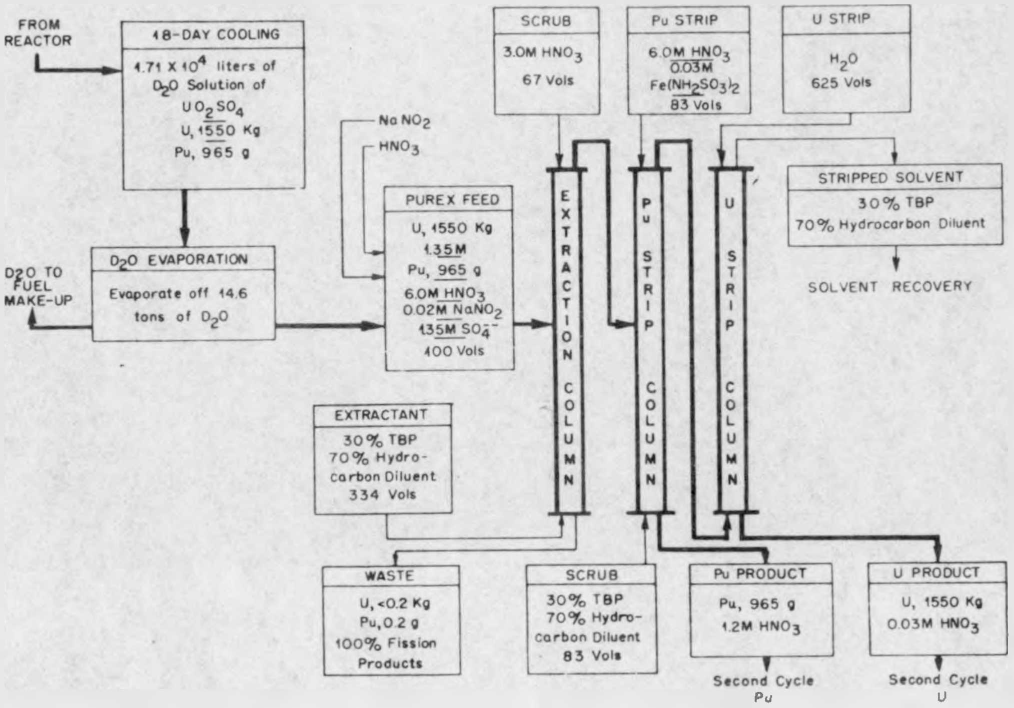


Fig. 1—Processing of material from the homogeneous plutonium producer. Basis: uranium, 1550 kg/day; plutonium, 965 g/day.

The use of tributyl phosphate for uranium and plutonium recovery has received extensive evaluation, and losses of less than 0.1 per cent for both elements are readily attainable in each solvent extraction cycle.[3,4] The required separation of uranium and plutonium from fission products, and from each other, can be obtained in two cycles. The major uncertainty associated with this solvent-extraction scheme is the obtainment of adequate plutonium recovery in the presence of sulfate ion.

The mechanism of plutonium extraction by the tributyl phosphate involves the plutonium(IV) ion as follows:

$$\mathrm{Pu(NO_3)}_n^{4-n}\ \mathrm{(aq)} + (4-n)\ \mathrm{NO_3^-}\ \mathrm{(aq)} + 2\mathrm{TBP\ (org)} \rightleftharpoons \mathrm{Pu(NO_3)_4(TBP)_2(org)}$$

In solutions containing sulfate ion, tetravalent plutonium is strongly complexed, and the extractable plutonium nitrate ion exists in equilibrium with the undissociated and inextractable plutonium sulfate

$$\mathrm{Pu(NO_3)}_n^{4-n}\ \mathrm{(aq)} + x\mathrm{SO_4^{--}} \rightleftharpoons \mathrm{Pu(SO_4)}_x^{4-2x}\ \mathrm{(aq)} + n\mathrm{NO_3^-}\ \mathrm{(aq)}$$

By the addition of nitric acid to the system, this equilibrium may be displaced in favor of the solvent-extractable plutonium nitrate. In the proposed system the mole ratio of sulfate ion to uranium is unity. Good uranium and plutonium recoveries have been demonstrated in the Oak Ridge National Laboratory's metal-recovery operations where the mole ratio of sulfate ion to uranium was 0.24. At Knolls Atomic Power Laboratory, under conditions similar to those proposed here, uranium recovery of greater

DECLASSIFIED

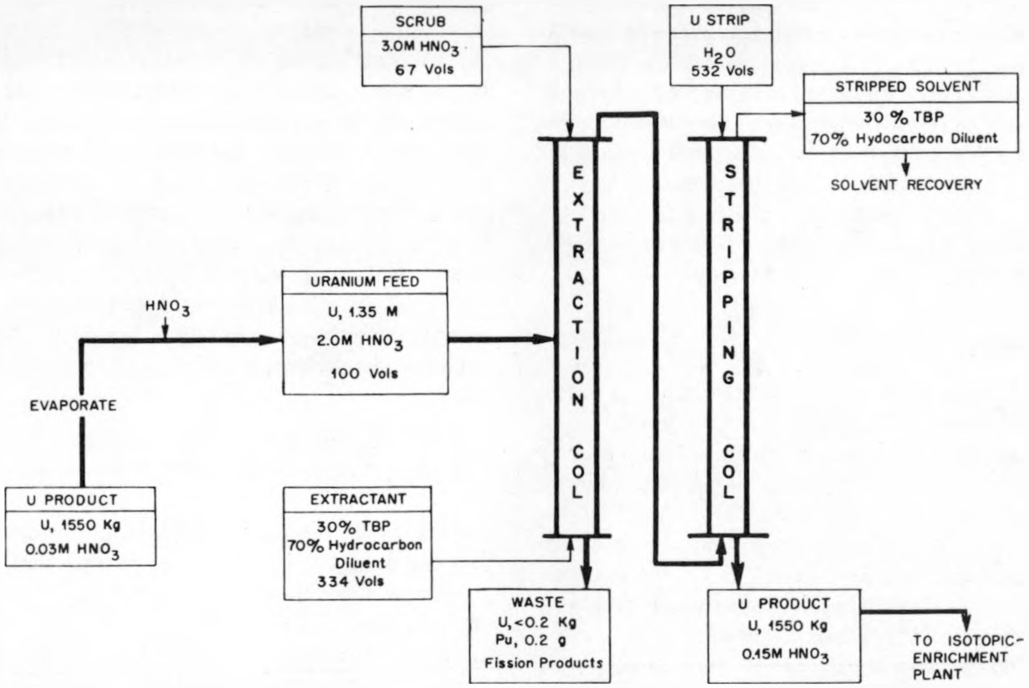


Fig. 2—Processing of material from the homogeneous reactor; second uranium cycle.

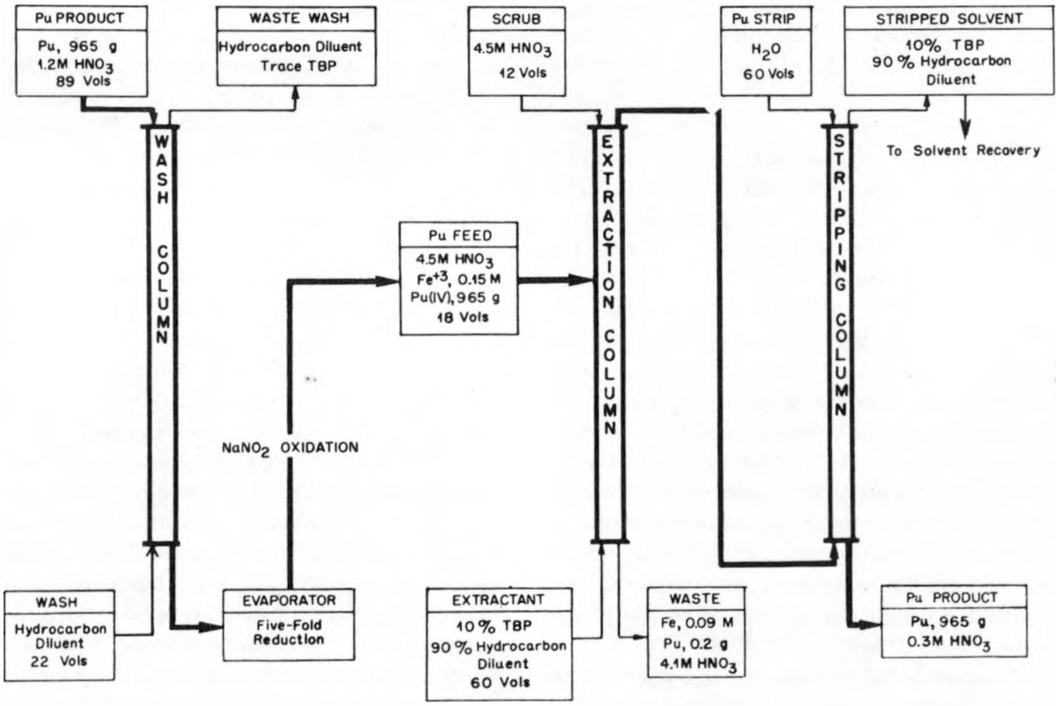


Fig. 3—Processing of material from the homogeneous reactor; second plutonium cycle.

DECLASSIFIED

than 99.9 per cent in TBP extraction was obtained at a 48 mole ratio of sulfate ion to uranium.

Some uncertainty arises from the short cooling time which is proposed in this scheme since the behavior of short-lived fission products, such as iodine, in tributyl phosphate extraction is unknown. This problem is simply alleviated, at the expense of greater fuel inventory, by increasing the cooling time to 90 days.

U^{233} Breeder

At the present time the most probable breeder is one which operates with a U^{233}-solution core surrounded by a blanket of thorium oxide slurry containing 1000 g of thorium per liter in heavy water. If the core of this reactor is 10 ft in diameter, then the blanket must contain about 40 tons of thorium for less than 1 per cent neutron loss. For such a reactor, operating at about 600 megawatts, a reasonable chemical processing period is about 650 days. The capacity of the blanket-processing plant for this reactor would be about 60 kg of thorium per day, and the U^{233} output would be 715 g. Of this 715 g, 605 g must be returned to the reactor core for fuel. The rate of processing of the U^{233} in the core depends on the amount of fission-product poison that can be tolerated. This is not yet known for such a reactor.

The first step in the processing of both core and blanket would consist in heavy water removal and conversion to a light water system. The processing of the U^{233} core would be similar to that described for the plutonium producer, but on a much smaller scale.

The thorium oxide blanket, containing U^{233}, Pa^{233}, and fission products, would be cooled for eight months to permit the decay of Pa^{233} to U^{233}. The thorium oxide would then be dissolved in boiling 16M nitric acid containing 0.05M hydrofluoric acid catalyst.[5] U^{233} separation from thorium and fission products would be effected by solvent extraction using either methyl isobutyl ketone or tributyl phosphate as the solvent. A U^{233} recovery of 99.9 per cent would be obtained in the one solvent-extraction cycle required for separation from fission products. The methyl isobutyl ketone process has been demonstrated at ORNL during a program[6] which recovered 350 g of U^{233}, but it is felt that a similar tributyl phosphate extraction process, although undemonstrated, would be feasible and more desirable.

The fertile thorium would finally be recovered by solvent extraction with tributyl phosphate, using nitric acid as the salting agent. Thorium recoveries of 99.9 per cent are indicated from laboratory work,[7] and one solvent-extraction cycle would provide adequate separation from fission products. Finally, the thorium nitrate would be decomposed, by heating, to thorium oxide for reuse. Figures 4 and 5 show the suggested processing scheme for a U^{233}-breeder blanket of thorium oxide slurry.

PRESENT STATUS OF CHEMICAL PROCESSES FOR ALTERNATE SYSTEMS

A number of alternates are being considered for the uranyl sulfate fuel in the plutonium producer and for the thorium oxide of the breeder. These alternates are being investigated primarily because they offer advantages for obtaining useful power from the reactor or because they have more desirable nuclear properties.

Plutonium Producers

1. $UO_2(NO_3)_2$ System. The efficient operation of a plutonium producer employing uranyl nitrate as fuel would necessitate the use of N^{15} in the nitrate ion since naturally occurring nitrogen has an excessively high neutron-capture cross section. N^{15}, produced at present by a chemical-exchange reaction in the NH_3-NH_4^+ system, is prohibitively expensive for serious consideration. However, more promising systems are now being investigated and may yield an economically feasible source of this isotope. The processing schedule and cooling requirements of this system would be similar to those of the uranyl sulfate reactor. Removal of heavy water and N^{15} from the fuel would constitute the first step in the chemical processing. In this case evaporation of the fuel would yield, first, anhydrous uranyl nitrate and, finally, uranium trioxide. Heavy water and $DN^{15}O_3$ would be obtained as condensate for reuse in the make-up of a fresh fuel batch. The production of uranium trioxide is well established in Atomic Energy Commission technology, and it seems certain that very low heavy water and N^{15} losses could be realized since uranium trioxide is now pro-

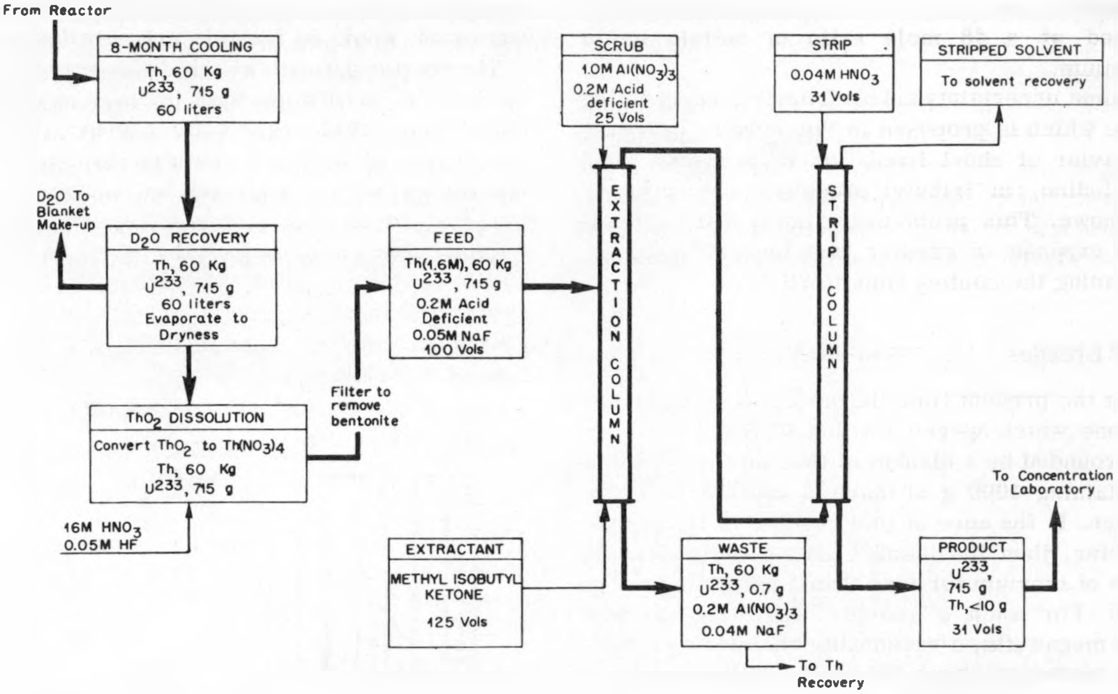


Fig. 4—Recovery of U^{233} from ThO_2 in U^{233}-breeder processing. Basis: thorium, 60 kg/day; U^{233}, 715 g/day.

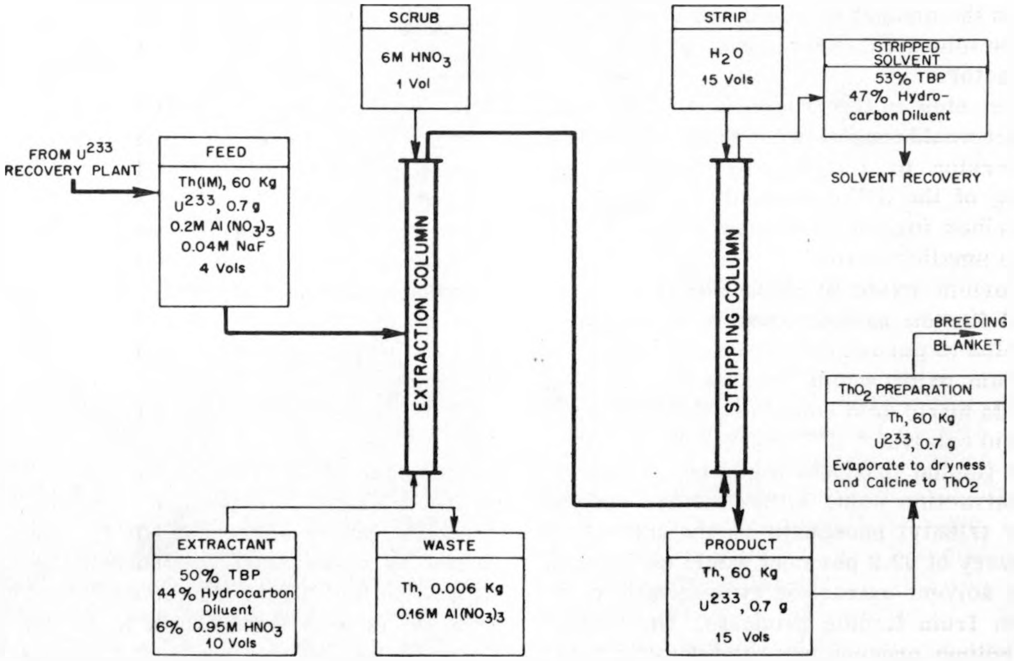


Fig. 5—Thorium recovery and decontamination in U^{233}-breeder processing. Basis: thorium, 60 kg/day.

DECLASSIFIED

duced routinely and in large quantities, containing 0.1 and 0.6 wt. % water and nitric acid, respectively.

The decomposition of uranyl nitrate yields nitrogen dioxide, necessitating the addition of oxygen and heavy water to form $DN^{15}O_3$. The conversion of nitrogen oxides to nitric acid is a problem which is now being investigated extensively in connection with fumeless uranium-nitrate with nitric acid and decontaminated by the standard Purex process (see Fig. 6).

2. UO_2F_2 System. The chemical processing of the uranyl fluoride system presents no unusual difficulties that have not already been discussed in connection with uranyl sulfate and uranyl nitrate. It is felt that the most satisfactory removal of heavy water could be accomplished by evaporation to uranium trioxide, using the condensate from this step for make-up of fresh fuel. This evaporation is a difficult one from the standpoint of obtaining a satisfactory corrosion-resistant material, and considerable research along this line would be required.

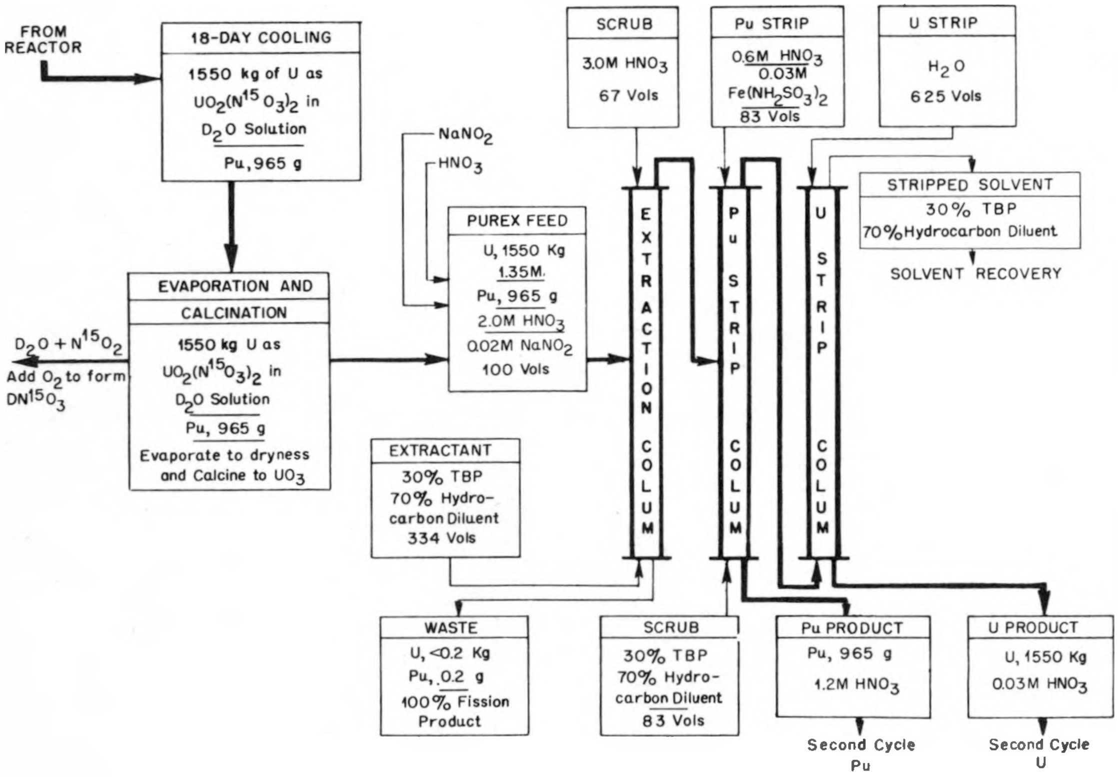


Fig. 6—Chemical processing of material from UNH-fuel plutonium producer. Basis: uranium, 1550 kg/day; plutonium, 965 g/day.

dissolving procedures. In a short time considerable data on the recovery of the oxides of nitrogen should be available.

The principal problem associated with the foregoing proposal lies in the development of suitable equipment for calcining highly radioactive materials. Considerable progress has been made along this line at KAPL, where a drum dryer for converting highly radioactive liquid wastes to powders was investigated.

Having obtained the uranium in the form of uranium trioxide, it is easily converted to uranyl

If appreciable fluoride ion was present in the solvent-extraction feed, considerable complexing of tetravalent plutonium, as the inextractable fluoride, would occur. This difficulty has been successfully alleviated in the past by formation of the stable fluoaluminate ion on the addition of excess aluminum nitrate to the system. In the worst case so much aluminum nitrate, 4 moles per mole of fluorine, might be necessary that this system would appear quite unattractive from a processing standpoint.

3. Slurry Fuels. One promising fuel for a homogeneous plutonium producer consists of a slurry of uranium trioxide stabilized by bentonite, an insoluble, complex aluminum silicate. The first step in the processing of such a fuel would be evaporation for heavy water removal. The uranium in the cake would be dissolved in nitric acid, and the bentonite would be removed by filtration. Finally, the Purex process would be employed for decontamination of uranium and plutonium.

A serious problem in the chemical processing of slurry fuels stabilized with bentonite arises from the fact that bentonite contains about 5 per cent water of constitution. It seems likely that exchange would occur between protium and deuterium. Subsequent recovery of the deuterium would undoubtedly be difficult. This problem requires further study.

Bentonite also possesses ion-exchange properties, and appreciable quantities of plutonium and uranium would undoubtedly be adsorbed on the material. If bentonite proves to have adequate chemical and radiation stability, it may be used repeatedly as a stabilizer for fresh fuel batches, and the problem of uranium and plutonium holdup is not a serious one. If it does not possess sufficient stability for reuse, a method for quantitatively eluting these ions must be developed.

At the present time slurries that do not require bentonite stabilization are under development. Should this program prove successful, the chemical-processing problems introduced by the presence of bentonite would be eliminated.

U^{233} Breeders

1. $Th(NO_3)_4$ Blanket. A satisfactory thorium nitrate breeding blanket would necessitate the use of N^{15} in the anion. It is felt that with this system the solvent extraction of the U^{233} could be carried out in a deuterated-N^{15} system which would leave the thorium unaltered for return to the blanket. A small amount of deuterium and N^{15} would follow the U^{233} into the solvent, but it seems likely that by using a deuterated water strip the recovery of both heavy water and N^{15} from the small amount of U^{233} would be simpler than making the same recovery from the bulk thorium.

2. Fused-salt Blanket. The development of a fused-salt breeding blanket is now under way. A satisfactory system should have a melting point of about 300°C and contain greater than 1000 g of thorium per liter; the ratio of neutron-capture cross section for thorium to total other constituents should exceed 10. If a satisfactory system is found, it will probably be a melt of ThF_4 and one or more of the following: BeF_2, AlF_3, BiF_3, PbF_2, MgF_2, Li^7F, and ZrF_4. The chemical processing of this blanket would consist in periodic U^{233} removal and less frequent separation of thorium from fission products. At the present time the most certain, although unwieldly, method of handling this problem appears to be the conversion of the fluoride melt to an aqueous system by the addition of excess aqueous aluminum nitrate to complex the fluoride ion. The U^{233} would then be recovered by hexone extraction, and the thorium would be decontaminated by extraction with tributyl phosphate. Both of these processes have been described previously. It is to be emphasized that the only merit to this scheme is that it almost certainly is workable; many more sophisticated, but untried, approaches are obvious.

PROSPECTS FOR IMPROVED HOMOGENEOUS-REACTOR PROCESSING

The processes previously proposed for handling reactor systems were selected as those appearing to be most certain of success in the present state of our knowledge. In every case the process presented has serious disadvantages. The purpose of this section is to describe processing techniques which will substantially better the position of homogeneous reactors for plutonium production and breeding.

Plutonium Producers

It was previously indicated that Pu^{240} build-up determines the processing frequency in the case of a plutonium producer. If a method for continuously removing plutonium and fission products were available, the reactor could then be operated until enrichment of the fuel was necessary and the equivalent of the entire loading subjected to decontamination from fission prod-

DECLASSIFIED

ucts every 31 days instead of every 12 days. This change in the quantity of uranium handled assumes a higher enrichment of feed to the reactor than the previous case. One of the most promising development fields in homogeneous-reactor processing therefore is the continuous removal of plutonium from the fuel without otherwise altering its composition. A second field of effort which is being pursued is the removal of high-cross-section fission products.

Solvent extraction by the Purex process appears at the present time to be the optimum method for decontaminating uranium sufficiently to permit its return to a diffusion plant.

1. Ion-exchange Applications. An ion-exchange process[8] for the separation of plutonium from uranium and fission products reached a high state of development at the Chicago and Clinton laboratories as an alternate to the bismuth phosphate process. When a homogeneous reactor was being considered in 1945 at the Clinton laboratories, the inherent advantages of ion exchange as a means of continuously decontaminating the fuel solution were recognized.[9] More recently a program has been under way in the Chemical Technology Division at ORNL to study the application of ion exchange to the homogeneous-reactor processing problem. This program has evaluated several ion exchangers, both organic and inorganic, for their ability to adsorb fission products. It has been shown that organic exchangers are probably sufficiently stable toward radiation for use in the processing problem at hand and that all the high-cross-section nongaseous fission products may be removed by ion exchange.

A number of exchange materials have been evaluated for their ability to remove fission products from uranyl sulfate solution, and it has been found that the use of a three-adsorbent system yields essentially complete removal of fission products. The optimum adsorbents are as follows: fuller's earth, which removes zirconium, niobium, and cesium; Dowex-50 cation exchanger, which removes plutonium, the rare earths, strontium, and barium; and Dowex A-1 anion exchanger, which removes molybdenum, ruthenium, and tellurium. For a plutonium producer, only a Dowex-50 bed, removing plutonium and high-cross-section fission products, would be required.

A serious problem confronting the use of ion exchangers is the relative instability of these synthetic organics in very high radiation fields. A program designed to obtain a quantitative evaluation of radiation effects on the exchange capacity of organic resins is now under way. Samples of Dowex-50 irradiated in the 1500-curie Co^{60} source showed a linear decrease in adsorption capacity with respect to exposure time. For each kilowatt-hour of radiation absorbed per kilogram of resin the material lost 10 per cent of its ion-exchange capacity. This radiation effect is not excessive for the homogeneous-reactor processing which is now visualized. For example, to maintain a fission-product concentration equal to 1 per cent of the U^{235} in the HRE, 5 per cent of the fuel would be processed per day after one day of cooling. This batch would be processed in 1 hr, through a 17-g Dowex-50 resin bed. The radiation damage to the resin would be equivalent to about 1.2 kw-hr per kilogram of resin, or it would decrease the exchange capacity by only 12 per cent. This effect is of the same order of magnitude as that expected in an actual plutonium producer employing a correspondingly larger bed.

There has been operating experience at ORNL in the use of ion-exchange resins at the high radiation levels encountered in the radiobarium production process.[10] In a pilot-plant run involving the adsorption of 6700 curies of gross activity on a Dowex-50 resin column, the resin was irradiated to the extent of 1.8 kw-hr/kg. Radiation damage in this case destroyed about 20 per cent of the ion-exchange capacity; however, in a subsequent separation of barium and strontium no unusual effects were observed. In the future, ion-exchange purification will be employed routinely for producing 10,000-curie batches of radiobarium at ORNL. This processing involves resin that receives damage which is equivalent to 0.6 kw-hr per kilogram of resin. In view of the foregoing experience and the radiation damage data, ion exchange may be expected to play a useful role in homogeneous-reactor processing. At the same time much more information on radiation stability is required before we may feel safe in exploiting ion exchange fully at high fission-product concentrations.

Figures 7 and 8 show the type of chemical processing, coupling ion exchange with Purex,

DECLASSIFIED

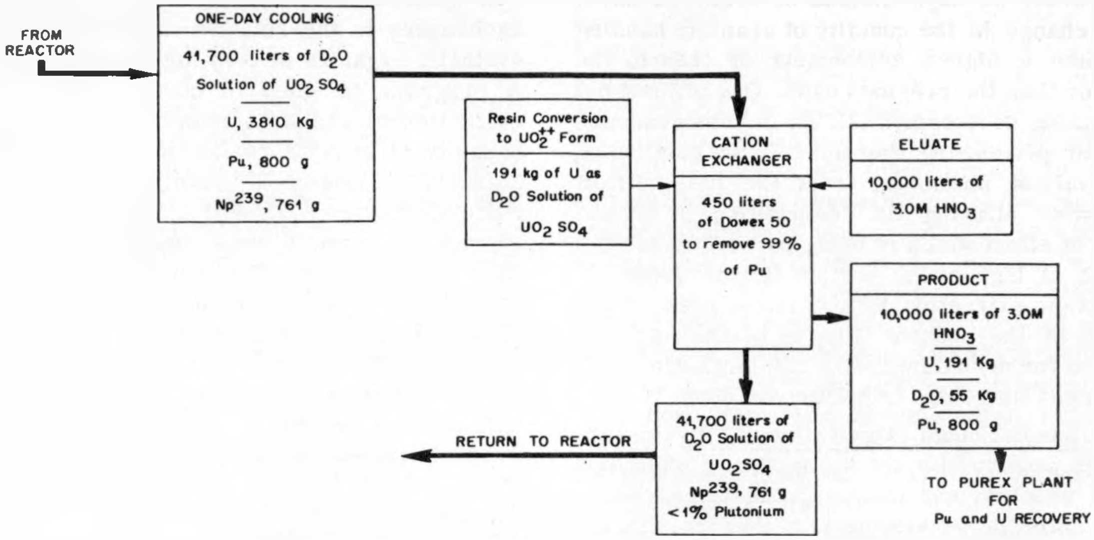


Fig. 7—Chemical processing of material from homogeneous plutonium producer; continuous plutonium removal by ion exchange. Basis: uranium, 3810 kg/day; plutonium, 800 g/day; neptunium, 761 g/day (passed to ion exchange).

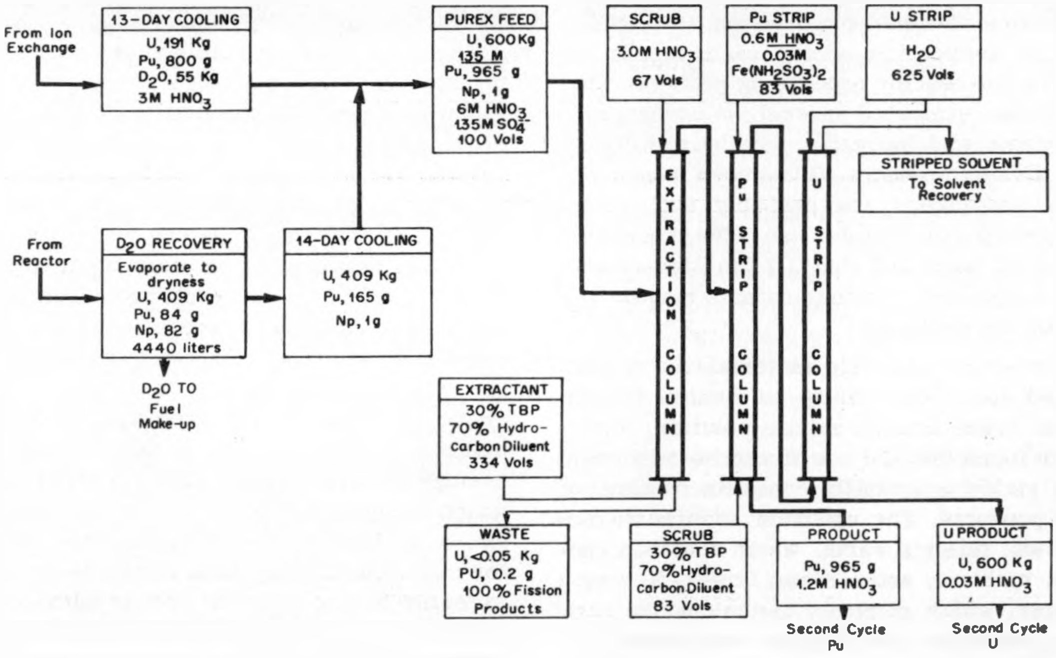


Fig. 8—Chemical processing of material f homogeneous plutonium producer; plutonium and uranium recovery. Basis: (from ion exchange) uranium, 191 kg day; plutonium, 800 g day; (from the reactor) uranium, 409 kg/day; plutonium, 84 g/day; neptunium, 82 g/day.

DECLASSIFIED

which is visualized for the homogeneous plutonium producer. By including an ion-exchange cycle for plutonium removal and by using higher feed enrichment, it is possible to employ a 31-day processing cycle instead of a 12-day cycle for the uranium which must be decontaminated prior to reenrichment. Each day 3810 kg of uranium would be withdrawn from the reactor, cooled one day, and passed through an ion-exchange column, where plutonium and fission products would be removed.

The ion-exchange cycle would employ Dowex-50 resin previously placed in the uranyl form by regeneration with a heavy water solution of uranyl sulfate. Consequently, only plutonium and fission products would be removed from the fuel, and uranium from the resin would be added to it. The effluent uranyl sulfate solution from the ion-exchange column would be returned to the reactor without further chemical treatment. At the end of the adsorption cycle the resin would contain essentially all the plutonium and cationic fission products plus about 191 kg of uranium and 55 kg of heavy water. These materials would then be eluted from the column with nitric acid and combined with 409 kg of uranium, taken directly from the reactor and separated from the heavy water. This solution would comprise the feed to the solvent-extraction plant and would contain 600 kg of uranium, 884 g of plutonium, and 82 g of Np^{239}. Following 14 days of cooling to permit decay of the Np^{239}, this solution would be fed to the Purex plant where uranium and plutonium would be extracted with tributyl phosphate. The solvent extract would then pass to a second column where plutonium would be removed in a reducing strip solution. Finally, uranium would be stripped from the solvent with water and sent through a second tributyl phosphate extraction cycle for further decontamination before it is returned to the enrichment plant. The plutonium would then be further purified in a second tributyl phosphate extraction cycle carried out in small critically safe equipment.

The economy of plutonium recovery by an ion-exchange solvent-extraction recovery process will depend heavily on the deuterium losses which are encountered. Ion-exchange resins contain three types of hydrogen: (1) that which is present as an integral part of the molecule, such as benzene, methylene, and hydroxyl hydrogen; (2) that which is loosely bound (water of gelation); and (3) that which occupies an exchangeable position. The last source of hydrogen may easily be eliminated from a processing system by utilizing the resin in the uranyl form. Exchange between deuterium and protium in Amberlite IR-1 resin, which contains about 6 per cent constitutional hydrogen and about 15 per cent water of gelation, has been investigated.[11] It was found that exchange took place rapidly and completely between the water of gelation and heavy water but that no constitutional protium was involved in the exchange. Since water of gelation is easily removed by heating the resins, there is a good possibility that ion exchangers may be employed in deuterated systems with very low losses of deuterium. This work on protium-deuterium exchange in organic resins should be extended, particularly to include anion exchangers where there is reason to believe the picture may not be so optimistic.

The successful removal of plutonium and fission products from the reactor by ion exchange is dependent upon their being present as ionic species. In the proposed fuel system, at a pH of 2, there is a strong likelihood that plutonium would polymerize or hydrolyze. Fortunately tetravalent plutonium is complexed strongly by sulfate ion, and this reaction tends to inhibit polymerization or hydrolysis. It is not possible at present to accurately predict the net effect of these forces, and a program aimed at determining the chemical form of plutonium and fission products in the fuel should be instigated.

2. Thenoyl Trifluoroacetone Extraction. The chelate compounds formed between thenoyl trifluoroacetone (TTA) and many metals have been studied extensively, and a solution of this reagent in benzene has been proposed as a solvent for separating plutonium from uranium and fission products. TTA extraction offers an excellent method for removing plutonium from the reactor solution; however, there is little possibility that the desired elimination of high-cross-section fission products could be effectively accomplished by this means. Nevertheless the feasibility of employing TTA should be explored more fully, particularly for final cleanup of the plutonium obtained from the ion-exchange column.

3. Electrolysis. Electrolytic techniques for removing plutonium and fission products from

DECLASSIFIED

homogeneous-reactor systems are attractive since radiation-damage problems are minimized and process-reagent costs are extremely low. The electrolytic precipitation of a small amount of uranium has been used successfully to remove rare earths and plutonium from a sodium bicarbonate solution.[12,13] The passage of fuel solution through a diaphragm cell in which a high uranyl-ion concentration would be reached results in the precipitation of a small amount of uranium. This precipitate carries plutonium and the rare earths almost quantitatively. The simple electrolysis of uranyl sulfate containing fission products has resulted in good removal of iodine, ruthenium, and molybdenum. Finally, it seems likely that certain fission products, such as cesium, could be effectively separated from uranium by electromigration through a diaphragm into a separate cell compartment. Electrochemical methods of separating reactor products appear very promising from the standpoint of low cost and minimum waste disposal and should be investigated further. The chief obstacle confronting electrolytic operations for handling radioactive materials at the present time is felt to be the lack of project experience.

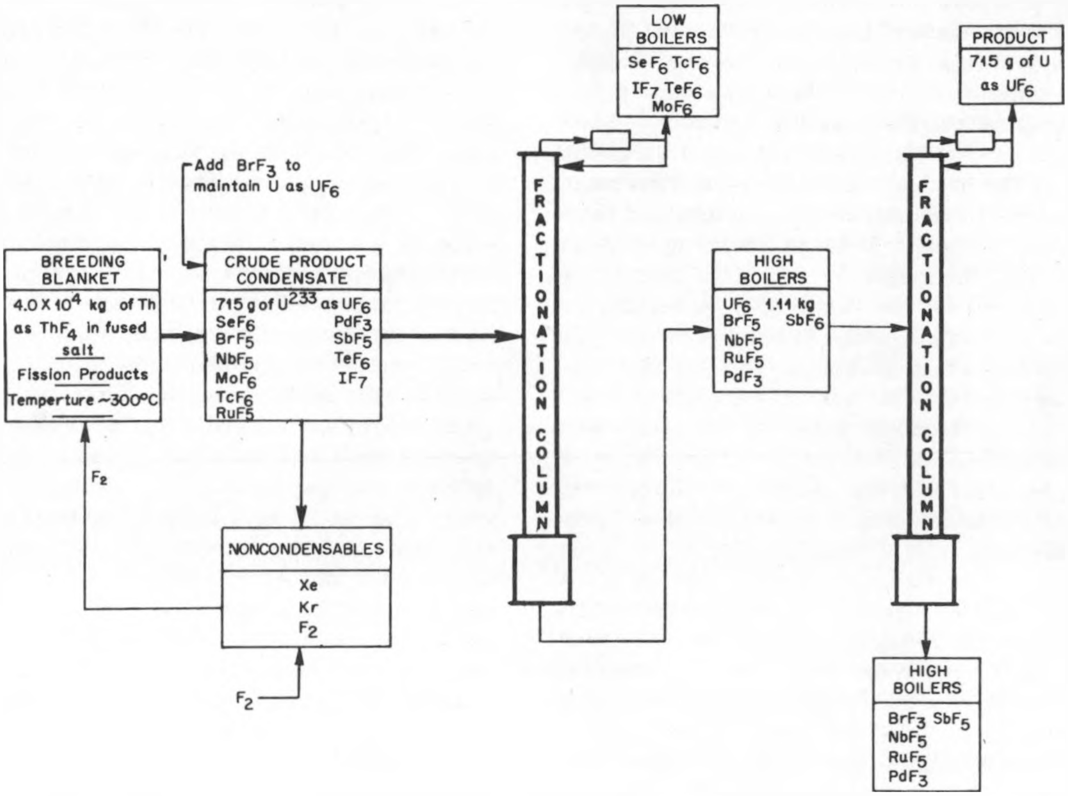


Fig. 9—Volatilization recovery of U^{233} from a fused-salt breeding blanket. Basis: continuous removal from blanket of 715 g/day of U^{233}.

U^{233} Breeders

Volatilization of uranium hexafluoride from a fused-salt breeding blanket offers an attractive processing possibility for an otherwise difficult system. On bubbling fluorine gas through the fused-salt blanket, the fluorides of uranium, selenium, bromine, krypton, niobium, molybdenum, tellurium, ruthenium, palladium, antimony, iodine, and xenon would be removed almost completely since their boiling points are near or below 300 C. Zirconium, rhodium, and indium would be partially removed at the column head, and the other elements having high boiling

DECLASSIFIED

points would be removed from the still pot. This process is shown in Fig. 9. Some special type of equipment may be needed to keep the uranium losses low.

CONCLUSIONS

The previous discussion has pointed out that our present state of knowledge does not permit the unqualified proposal of those processes which contribute most to the ultimate simplicity of homogeneous reactors as fissionable-material producers. This results from the fact that most of the process systems and requirements are unique to homogeneous reactors and there has been little cause in the past to examine them. In general, the major uncertainties involve radiation stability, the handling of deuterium and N^{15} contaminated with fission products, the chemical state of plutonium formed in homogeneous reactors, the solvent-extraction chemistry of short-cooled material, the chemistry of neptunium, and the chemistry of bentonite. It is felt that a large portion of future process development should be expended on these problems.

The effect of radiation on ion-exchange resins determines how long fuel must be cooled before plutonium and fission products are removed. This cooling inventory influences the over-all economy of reactor operation. Similarly, it is conceivable that the stability of tributyl phosphate will determine the minimum cooling time before fuel processing. It is therefore important that quantitative data on the effect of radiation on organic exchangers and organic solvents be obtained. A comprehensive program employing the Co^{60} source, Van de Graaff irradiations, and the actual reactor exposures should be initiated soon. At the conclusion of this study it should be possible to define quite closely the highest radiation levels to which ion-exchange resins and organic solvents may be subjected and still retain their process usefulness. A similar study evaluating gasketing material, protective coating, and plastics should also be conducted.

Much information is needed on the handling of deuterium and N^{15}. Methods of removing them from pertinent fuels should be developed, and reliable data should be obtained on the losses that may be expected. The engineering problems involved here are formidable since many of the systems employ highly corrosive materials. The engineering program should be carried out concurrently with the chemistry studies. In addition, the exchange reactions between protium and deuterium in ion exchangers and organic solvents should be investigated and thoroughly understood if these materials are to be used extensively.

The economics of plutonium production in homogeneous reactors is significantly enhanced by the continuous removal of plutonium and fission products. Since there is some doubt that plutonium exists in an exchangeable ionic form in this system, considerable effort should be made to establish its true state as soon as possible. In the event that it is found not to be ion exchangeable, methods of converting it to a satisfactory form need to be investigated. This same consideration should be applied to the high-cross-section fission products.

Most available data on the separation of uranium and plutonium from fission products have been obtained with material cooled for 100 days. In homogeneous-reactor processing a cooling time of about 18 days is adequate for the decay of neptunium. The effectiveness of solvent extraction for decontaminating short-cooled material should be studied, and the cooling time should be correlated with the efficacy of the separation of uranium and plutonium from fission products. If certain short-lived fission products impair the processing of relatively young material, specific measures should be devised for their removal.

Present thinking on plutonium-producer processing includes a decay period for the conversion of neptunium to plutonium. Radiation stability and solvent-extraction efficiency permitting, this cooling time could be reduced, with an attendant decrease in fissionable-material inventory provided neptunium could be recovered with plutonium in the Purex processing. There are meager data which indicate that neptunium may be made to follow plutonium in the Purex process. A study should be instituted on the solvent-extraction chemistry of neptunium with the foregoing objective in mind.

The most promising uranium and thorium slurries that have been found to date employ bentonite as a stabilizing agent. A relatively minor program aimed at evaluating the protium-deuterium exchange reactions of bentonite should

DECLASSIFIED

be undertaken. In addition, methods of eluting uranium and plutonium from the bentonite exchange positions should be sought.

The problems which have been mentioned are serious ones which deter the use of the optimum processing schemes for homogeneous reactors. The time schedule that the solution of these problems follows is only slightly less important than their ultimate solution. If the HRE is demonstrated to be operable, there is a strong likelihood that the decision will be made soon thereafter to build a large-scale homogeneous plutonium producer which may be of intermediate power level. Consequently, chemical-processing developments should be paced by the HRE, and every effort should be made to have an integrated process for plutonium recovery developed to the point where its essential features may be evaluated in the HRE soon after start-up. Therefore it is concluded that every effort should be made to obtain fairly definitive answers to all the above problems within the next year.

ACKNOWLEDGMENT

The author thanks Don E. Ferguson for his many valuable suggestions and calculations of reactor processing periods and gratefully acknowledges the assistance of Frank L. Steahly in preparing this article.

REFERENCES

1. J. W. Mellor in "Comprehensive Treatise on Inorganic Chemistry," Vol. XII, p. 103, Longmans, Green & Co., Inc., New York.
2. W. K. Eister, Recovery and Decontamination of Uranium 235 and Heavy Water from a Homogeneous Pile Slurry, June 1945 to January 1946, Report ORNL-648.
3. W. B. Lanham and T. C. Runion, Purex Process for Plutonium and Uranium Recovery, Report ORNL-479, Oct. 7, 1949.
4. W. B. Lanham and A. T. Gresky, Purex Process Laboratory Development, Report ORNL-717, June 15, 1950.
5. F. W. Schuler, F. L. Steahly, and R. W. Stoughton, The Dissolution of Thorium Metal and Thorium Dioxide in HNO_3-HF and HNO_3-$(NH_4)_2SiF_6$ Mixtures, Report CC-3576, Aug. 2, 1946.
6. D. E. Ferguson and E. L. Nicholson, Summary Report for the 23 Pilot Plant Program, Report ORNL-715, July 27, 1950.
7. D. C. Overholt, Recovery and Decontamination of Thorium from the Materials Testing Reactor, Report CF-49-11-211, Nov. 11, 1949.
8. J. A. Swartout, The Development of an Adsorption Extraction Cycle with High Decontamination, Report CN-3337, Dec. 10, 1945.
9. G. E. Boyd, The Possibility for the Purification of an Enriched Homogeneous Chain Reacting Solution by an Adsorption Cycle, Report CF-45-2-243, Feb. 19, 1945.
10. I. R. Higgins, R. E. Blanco, and W. E. Unger, Preliminary Demonstration of RaLa Ion Exchange Processes at Kilocurie Level, Report ORNL-623, Mar. 22, 1950.
11. A. W. Adamson and G. E. Boyd, Purification of Homogeneous Chain Reaction Solutions: Protium-Deuterium Exchange with Amberlite IR-1, Report Mon C-77, Apr. 2, 1946.
12. J. A. McLaren et al., The Electrochemical Recovery of Uranium and Fission Products from Two-Year-Old Hanford Metal Wastes, Report K-588, June 8, 1950.
13. J. A. McLaren et al., The Electrochemical Separation of the Rare Earths, Strontium, and Plutonium from Two-Year-Old Hanford Metal Waste, Report K-589, May 1, 1950.

October 1951

DECLASSIFIED

REACTOR FUTURES

An Engineering Test Reactor

By T. FAHRNER, R. L. STOKER, and A. S. THOMPSON

Atomic Energy Research Department
North American Aviation, Inc.
Downey, California

Report NAA-SR-Memo-32 (Del.)

PURPOSE OF REACTOR

The practice of using working models or pilot plants as experimental aids in designing and developing engineering equipment, machines, structures, and process plants is well recognized. In many applications the model or pilot plant may be fully developed functionally and may be capable of simulating simultaneously all the essential factors that are associated with the actual operation and performance of the full-scale facility under consideration. A model of this sort offers the final and most reliable means of appraising the performance, prior to actual construction and operation, of the prototype in question. To date this practice has not been exploited in designing and developing nuclear reactors, but the discussion here of the Engineering Test Reactor (ETR) indicates how this might be realized.

Criticality, which is peculiar to nuclear reactors, presents a problem in the achievement of small-scale working models of prototype reactors. If the most direct approach is taken to satisfy criticality, the result is simply the full-scale prototype. Thus, one is confronted with a large and expensive high-power installation rather than a relatively inexpensive low-power working model. The crux of the difficulty in obtaining a small working model of a nuclear reactor is, of course, the inability of a subcritical amount of neutron multiplying material to support its own leakage. It is the function of the proposed ETR to sustain the leakage from such subcritical models and thereby to provide conditions within the model approximating those which would exist if the model were operated with the remainder of its prototype. Stated another way, the purpose of the proposed reactor is to simulate the nuclear boundary conditions which would prevail over the subcritical specimen if the specimen were a part of the operating prototype under consideration.

Since the prime function of this proposed test reactor is merely to sustain a moderately high neutron-flux density throughout the test cavity to be occupied by scale models, considerable latitude is permitted in the reactor design. It is possible to keep the amount of critical materials, the cooling requirements, and the cost very small, as compared to full-scale isotope producers or high-power reactors, through the use of enriched fuel elements. Furthermore, this neutron-supporting reactor need not be remade for each working model tested. It can be a permanent facility in which a variety of working models, one at a time, can be inserted and tested. This will further reduce the cost per model test.

The ETR is viewed here as another useful experimental aid to the design and development of nuclear reactors. The approach should not be regarded as superseding such existing experimental aids as exponential and criticality experiments or any other component mock-up test of limited scope. Instead, the proposed attack is intended to close the rather large experimental gap existing at present between an exponential or criticality experiment of zero power and the full-scale high-power operating prototype.

Although the principal function expected of this reactor is to obtain the advantages of the working-model or pilot-plant concept in nuclear reactor development, there are also a number of other uses to which it could be put. Some of these uses are

1. Radiation damage studies
2. Investigation of radioactivity acquired by coolants

714 217

DECLASSIFIED

3. Studies of corrosion in the presence of nuclear radiation and neutron flux
4. Investigation of heat transfer from fuel elements for which out-of-pile mock-ups are inadequate or even impossible
5. Experimental isotope production

Table 1—Comparison of Six Engineering Test Reactor Configurations Having a 1-ft-diameter Test Hole

Moderator	Graphite	Graphite	D_2O	D_2O	D_2O	D_2O
Reflector:						
Material	Graphite	Graphite	D_2O	D_2O	Graphite	Graphite
Thickness, ft	1.3	1.5	1.3	1.5	1.5	1.6
Space density of U^{235},* g/cc	0.135	0.067	0.135	0.067	0.135	0.067
Core radius, ft	2.54	3.20	1.17	1.46	1.26	1.57
Core height, ft	5.0	6.4	2.0	2.6	2.2	2.8
Number of fuel rods	42†	67†	42‡	70‡	49‡	85‡
Weight of U^{235}, kg	8.2	8.3	1.75	1.88	2.27	2.50
Center-of-rod power, kw	152	179	51	64	54	67
Reactor power, megawatts	4.4	8.0	1.6	3.4	1.9	4.0
Average nv_{th}, neutrons/cm^2/sec	1.2×10^{13}	2.2×10^{13}	2.1×10^{13}	4.0×10^{13}	1.9×10^{13}	3.7×10^{13}
Peak nv_{th}, neutrons/cm^2/sec	2.3×10^{13}	4.6×10^{13}	3.3×10^{13}	6.3×10^{13}	3.2×10^{13}	6.1×10^{13}
Peak nv/average nv	1.87	1.90	1.56	1.56	1.66	1.66
Average power density in fuel, watts/g U^{235}	537	970	925	1780	840	1620
K_∞	1.70	1.47	1.79	1.61	1.81	1.61
L^2 (*thermal diffusion area*), cm^2	276	388	71	106	71	106
L_f^2 (slowing down area), cm^2	372	372	127	127	127	127
D_2O, metric tons			2.8	5.0	0.35	0.69

*U^{235} is assumed to be dispersed uniformly in aluminum, forming rods or slugs of Al-U^{235} alloy. (Equals 0.135 for natural U.)

†These Al-U^{235} alloy fuel rods are 1.36 in. O.D. and are sheathed with 0.040-in. thick aluminum, giving an over-all outside diameter of 1.44 in.

‡These Al-U^{235} alloy fuel rods are 1.00 in. O.D. and are aluminum sheathed giving an over-all outside diameter of 1.08 in.

GENERAL REQUIREMENTS OF REACTOR

The reactor proposed for serving the above function should have a centrally located test hole in order that the region of largest and most uniform neutron flux may be utilized. This test region should be large enough in cross section to allow the testing of a lattice of reasonable cell radius, and, at the same time, should be of sufficient length to prevent objectionable end effects. A vertical hole extending completely through the reactor seems preferable from the standpoint of ease of assembling the test specimen and its auxiliary equipment. Furthermore, destructive failure of the test specimen is less likely to cause serious damage to the reactor than it would in a horizontal test hole. The over-all size, cost, and cooling requirement of this supporting reactor increases with the test-hole size, but a through test hole not smaller than 1 ft in diameter would appear to be a satisfactory compromise inasmuch as this would accommodate the lattice of any reactor that has been suggested to date. In the example which follows, the bare core volume and reactor cooling would be increased about 60 per cent for the same neutron flux if a 2-ft test hole was used.

The ETR should be capable of supporting a fairly high neutron flux throughout the test region. It is believed that a flux intensity of at least 10^{13}, is desirable.

At higher neutron densities the cooling limitations associated with these cylindrical fuel rods would cause the necessary amount of critical materials and reactor cooling to be undesirably large even though enriched fuel is utilized.

Unquestionably, the design and construction can be facilitated and the cost of the reactor can be greatly reduced if it is basically one for which most of the design details have already been proved by actual operation. By making use of them, much time and effort that might otherwise go into designing and developing new fuel elements, control components, internal cooling schemes, etc., can be eliminated. Although the main function of this test reactor may be considered new, the reactor itself need not entail a host of new design details. Instead, it appears that a very useful test reactor can be designed around presently available, well-tried reactor components.

It is important that the amount of critical materials, the cooling requirement, and the cost of the proposed facility be commensurate with its utility. Preliminary study indicates that these requirements can be met

DECLASSIFIED

714 219

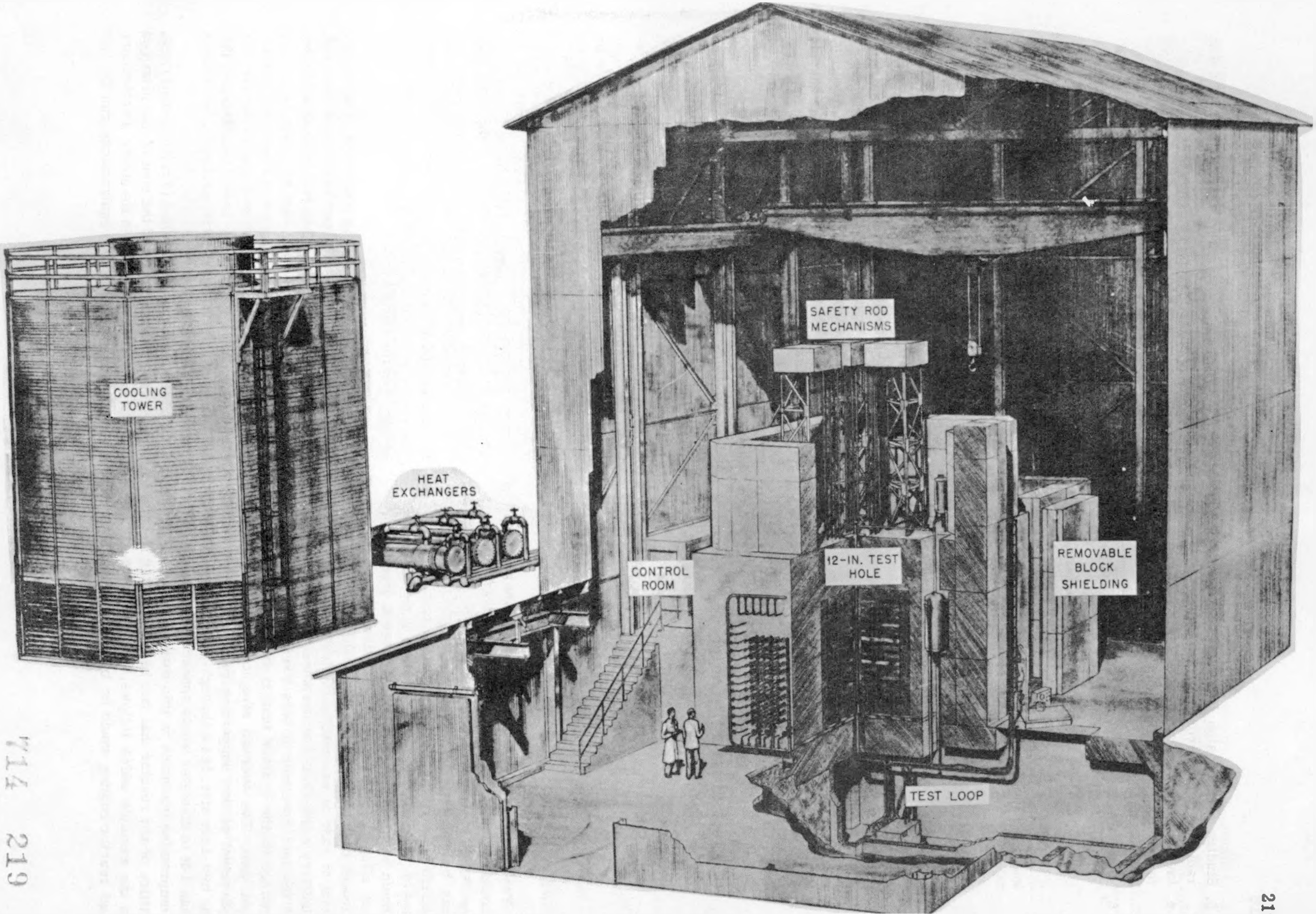


Fig. 1 — Engineering Test Reactor.

satisfactorily. Some consideration has been given to a number of possible reactor configurations; the results are given in Table 1. These tabulated results conform to the following assumed allowable cooling conditions for aluminum-sheathed fuel rods:

1. Cooling water inlet temperature = 85°F
2. Maximum allowable sheath temperature = 190°F
3. Cooling-water velocity = 25 ft/sec

Table 2 — Specifications for the Engineering Test Reactor

Basic idea	Reactor is to be constructed from parts which are now standard in AEC installations. This will result in a minimum of design effort, will eliminate the necessity for an extensive program of component development, and will permit a realistic estimate of cost and a short construction time
Reactor	Core is a 10-ft graphite cube (graphite blocks of Hanford W design) Contains 120 horizontal water-cooled fuel channels (Hanford W process tubes and fittings) Fuel is enriched U-Al alloy canned in aluminum (similar to that used in H pile) Critical mass is 8.3 kg of U^{235} Power is 8 megawatts nv_{th} average = 2.2×10^{13} (4.6×10^{13}, peak)
Cooling system	Recirculating, closed, distilled H_2O, with heat exchangers and cooling tower
Experimental facilities	At the center of the core there will be one 12-in. vertical hole in which experimental fuel rods or full-scale sections of reactor's can be tested. The rear shield is 10 ft thick and is used for fuel storage to permit adjustment of loading

Flexibility in the design of the reactor is important to the extent that some variation in the fuel distribution should be possible. This would permit testing a variety of reactor components comprising a wide range of K_∞. Also, two or more shielded regions adjacent to the shielded reactor might be provided so that one test could be assembled while another test was being run. This would reduce the change-over time between the testing of different models. More advanced or elaborate facilities to serve the intended purpose might be justified at some future date after experience has been derived from the one proposed. At present, however, a fairly simple, straightforward version is believed preferable.

EXAMPLE

As an example, Fig. 1 depicts an engineering test reactor for which the characteristics are approximately those of column 2 of Table 1. (Specifications for the ETR are shown in Table 2.) The rear shield, which is 10 ft thick, provides for adjustment of the loading as required for the particular test in progress. The fuel in any channel can be pushed out of the core and stored temporarily in the rear shield. Concrete-block shielding which can be handled by the crane is used around the test assembly and at the discharge face. The fuel rods are cooled by distilled water which is recirculated in a closed system through shell and tube heat exchangers. Heat is liberated to the atmosphere by means of water evaporation through an induced-draft cooling tower.

An estimate, based upon building costs for a research laboratory installation recently completed in the Los Angeles area, indicates that the complete unit, including reactor and control, reactor building, and cooling system, can be built for less than $2,000,000.

ACKNOWLEDGMENTS

In addition to helpful discussions with staff members, the writers wish to acknowledge calculating and design assistance from Edward Weisner, Hugo Richter, Frank Brady, and James Temple.

March 1951

TID 220

DECLASSIFIED

TECHNICAL NOTES

A NOTE ON THE DUCTILITY OF BETA URANIUM

By A. N. Holden

Knolls Atomic Power Laboratory
General Electric Company
Schenectady, N. Y.

Report KAPL-408

INTRODUCTION

Throughout the classified literature on the working of uranium, it is cautioned that the working of the metal in the beta phase be avoided.[1] Working in either the gamma or alpha phase has become routine practice, while the beta phase is avoided because of its brittleness. Beta uranium is not brittle per se, it is only less ductile than alpha or gamma. The working of uranium in the beta condition is not only feasible but has been done several times.

The evidence that beta-phase uranium is ductile is worthy of review in view of the widespread opinion that it is brittle.

Hardness measurements[2] have been made on uranium throughout the range of temperatures from room temperature up to the temperature of the gamma phase. In general, the results agree that beta at 700°C is no harder than alpha is at 500°C. These hardness data are plotted in Fig. 1. Alpha at 500°C can be worked readily. Therefore on the basis of hardness it would be predicted that beta should deform as readily.

Extrusion pressures have been measured by Arnold[3,4] for material extruded in the high alpha and beta temperature ranges. The beta phase at 700°C or above requires less pressure to extrude than alpha at 600°C. Between 650 and 700°C the beta phase (or more likely a mixture of beta and alpha) requires a somewhat higher pressure for extrusion than does alpha at 600°C. It is certain, however, that beta uranium is not brittle in extrusion. Some of the extrusion data collected by Arnold are shown in Fig. 2.

Compression tests[5] have been made on uranium at several temperatures from room temperature up to 750°C. The load required to deform 0.505-in.-diameter material 10 and 20 per cent in compression is shown in Fig. 3 for temperatures up to 750°C. These data indicate a ductility of at least 20 per cent for the beta phase. Furthermore, no greater pressure is required to deform beta uranium at 700°C than to deform alpha uranium at 500°C.

On a few occasions uranium has been rolled in the beta phase successfully. Bergson and Treco[6] have rolled uranium in the beta phase up to 61 per cent reduction without apparent difficulty. However, they carefully maintained their temperatures so that any particular pass was done with the material precisely at 700°C by reheating between passes. Beta uranium also has been rolled from 1.36 to 0.875 in. in diameter at Battelle.[7] However, it was found at Battelle that an initial billet temperature of 750°C was necessary to produce good beta-rolled rods. Lower or higher initial temperatures resulted in cracking. Uranium slugs have been rolled with finishing temperatures of 1250°F (677°C) or higher without difficulty.[8] While this material may not have been beta, it had the characteristic coarse grains of beta-worked material.

Recently Cooley[9] of the KAPL metal-working laboratory rolled a 0.500-in.-thick billet of uranium to about 0.040-in.-thick sheet at a temperature of 740°C. The material was carefully maintained in the beta phase by reheating between every pass. Reductions of about 15 per cent were made on each pass. The only difficulty experienced was the poor surface condition caused by excessive oxidation. Material that can be

DECLASSIFIED

rolled into sheet without jacketing and at reductions of 15 per cent per pass is ductile.

Further important evidence of the ductility of beta uranium has resulted from the ability to produce beta-phase single crystals that are stable at room temperature. These crystals, produced by slowly lowering uranium wires containing 1 atom % chromium through a temperature gradient from a gamma temperature to a beta temperature and quenching,[10,11] are very ductile. They can be readily bent to a small radius. Furthermore, they do not deform primarily by twinning at room temperature, as does alpha, but rather by slip. Alpha-phase single crystals when bent in the fingers produce a characteristic rasping sound due to the twinning. Beta-phase crystals deform without audible sound.

Metallographic evidence has substantiated the fact that beta crystals deform by slip. A comparison of the deformation markings on an alpha crystal with those of a beta crystal is shown in Fig. 4. Figure 5 is a macrograph of the same bent beta crystal which was shown in Fig. 4. The outer fibers in the bend were deformed about 15 per cent.

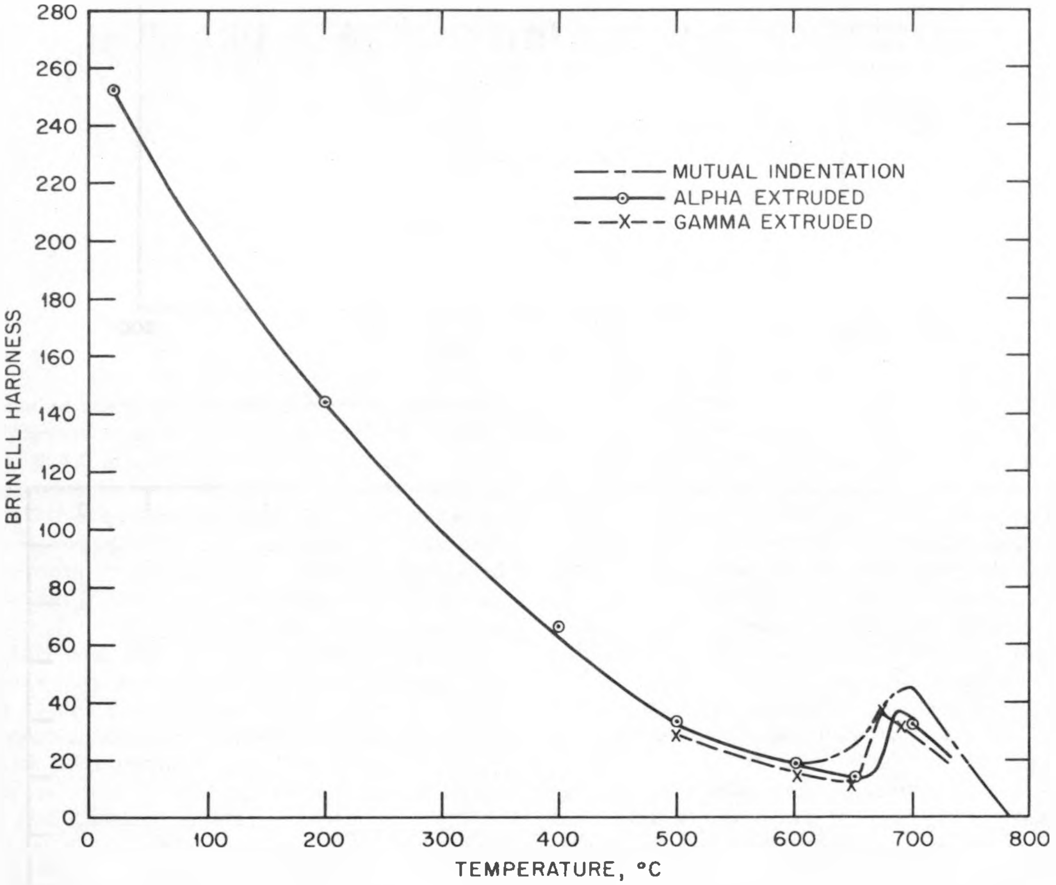


Fig. 1 — Hardness of uranium vs. temperature.[2]

DISCUSSION

Beta-phase uranium is ductile. The question is now asked, in the face of all the evidence that beta is ductile, why is it so often called brittle? The probable answer lies in the fact that frequently the attempts to work beta uranium have resulted in fracture of the material. However, only in those instances where beta uranium was worked with poor temperature control and was allowed to partly transform to alpha or gamma has failure occurred. The range in temperature over which beta is stable is small (660 to 770°C), and the usual commercial working does not hold readily within those temperature limits. Both the

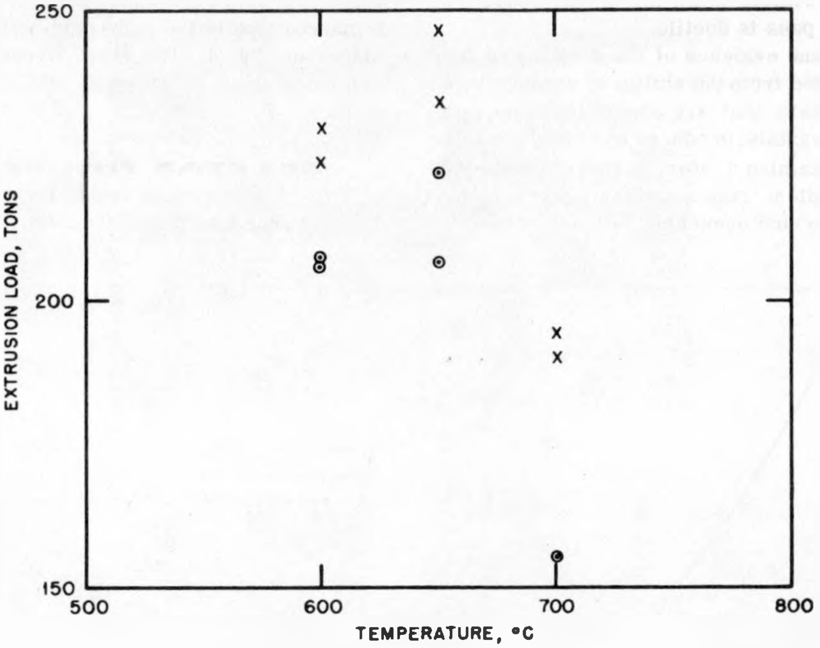


Fig. 2—Extrusion load vs. temperature for uranium.[3] ×, reduction ratio 16.7 to 1. ⊙, reduction ratio 8.5 to 1.

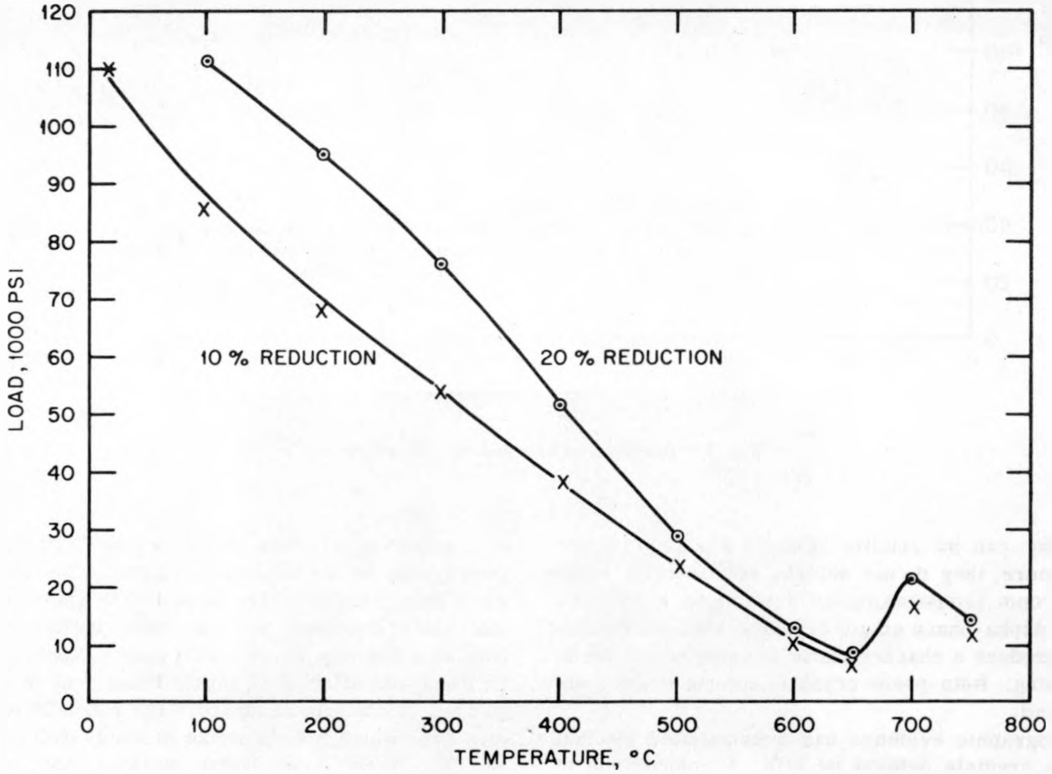


Fig. 3—Compression pressure vs. temperature for uranium.[3]

DECLASSIFIED

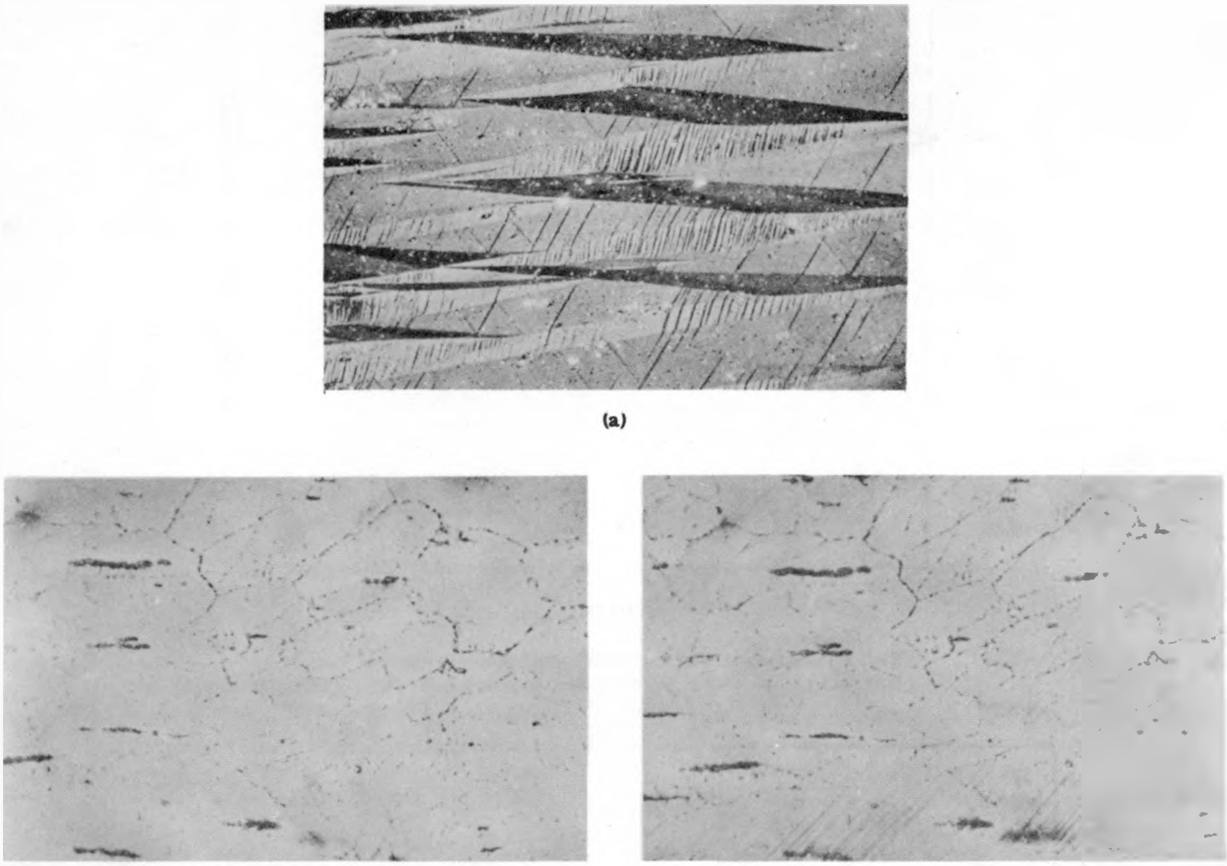


Fig. 4 — Deformation markings in alpha and beta single crystals. Beta crystals, as grown, show delineation of former gamma grain boundaries with precipitate particles. Slip bands cross through these boundaries with only slight changes in direction. (a) Twins in alpha. (Magnification 150×.) (b) Undeformed beta. (Magnification 100×.) (c) Slip lines in beta after deforming. (Magnification 100×.)

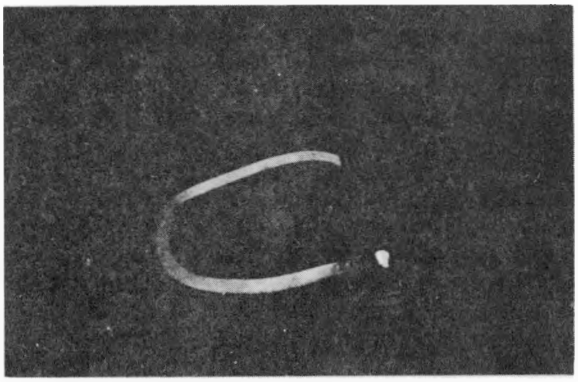


Fig. 5 — Bent beta crystal.

DECLASSIFIED

oxidation reaction and the energy expended in working tend to raise the temperature, while the interval between passes and the contact with cold rolls or dies tend to lower the temperature. If beta is to be worked, the working practice must be precise enough to maintain the temperature in spite of the variables tending to alter it.

The failure mechanism during the working of beta uranium which has partly transformed it to either alpha or gamma is not known, of course, but it is possible to speculate on how this might occur. Beta is many times harder than gamma at the transformation temperature (760 to 770°C). In fact, at the transformation temperature gamma has a yield stress of only 194 psi, while beta uranium has a yield stress of the order of 12,000 psi.[12] Suppose a small amount of gamma were to form at a few grain boundaries of an overheated bar of beta uranium that was being worked. Under these conditions it would be expected that all these gamma regions would fracture immediately under the stresses imposed, and the bar should literally fall apart. A similar effect might occur if the temperature of a bar worked in the beta range fell slightly below the beta-alpha transformation, although here the ratio of flow stresses (beta to alpha) is only a factor of 2 or 3 rather than 70 as for beta to gamma. More severe failures might be expected in working overheated beta than working undercooled beta simply because of the relative hardness of the transformation products. This is substantially what occurred in the beta-phase rolling performed at Battelle.[6]

If uranium were being worked in the high alpha range, on the other hand, the partial transformation of a few regions to the beta phase would probably not greatly affect the working of the material.

The foregoing concepts are admittedly qualitative, and the problem needs more detailed study. For example, there is reason, from metallographic evidence, to believe that beta crystals have only a few slip planes [perhaps only one (see Fig. 4)] and that they also have at least one good cleavage plane. If this is so, the material could well be brittle in the sense that zinc is brittle. Actually, if a coarse-grained cast zinc rod is bent, it breaks by cleavage, and this same phenomenon has been noted for polycrystals of quenched beta uranium.* Zinc, however, after careful preliminary cold working becomes extremely ductile and may be deformed at will. The same care in preliminary working may be necessary for beta uranium.

CONCLUSION

Beta uranium is not a brittle phase. It deforms readily by slip on at least one slip system. It may be hot-worked if reasonable care is taken to avoid transformations by accurate control of the temperature of working.

ACKNOWLEDGMENT

The author wishes to acknowledge the stimulating discussions with C. W. Tucker, J. E. Burke, and A. C. Cooley and to thank A. C. Cooley for working the uranium in the beta phase.

REFERENCES

1. Project Handbook, Report CL-697, p. 92.
2. Project Handbook, Report CL-697, Table 15, p. 35.
3. S. V. Arnold, Extrusion Characteristics of Uranium at 600, 650, and 700°C Billet Temperatures, Report MIT-1010, Oct. 11, 1948, pp. 24–26.
4. S. V. Arnold, Extrusion of Uranium, Report MIT-1018, May 6, 1949, pp. 38–42.
5. Progress Report, Report CT-2668, January 1945, pp. 7–16.
6. B. J. Bergson and R. M. Treco, Rolling of Uranium in the Alpha and Beta Phases, Report MIT-1010, Oct. 11, 1948, pp. 48–63.
7. Progress Report, Metallurgy, Battelle, Rolling Beta Phase, Report CT-2374, Nov. 1, 1944, pp. 254–259.
8. R. Teats, Fabrication of Slugs from Uranium Rolled at Different Finishing Temperatures, Report HW-12888, Mar. 30, 1949.
9. A. C. Cooley, unpublished research.
10. Research Report, Metallurgy, Report KAPL WJ-101, pp. 29–31.
11. Reactor Materials Report, The Effect of Structure on Nucleation in Solid-Solid Transformations of Uranium, Report KAPL-378, July 1950, pp. 12–17.
12. Cavendish Laboratory, Cambridge, The Yield Stress of Uranium at High Temperatures, Report BR-712, March 1949.

September 1950

---

*The procedure used to grow beta crystals involved slowly transforming 1 atom % chromium-uranium alloy wires from gamma to beta and quenching. Physical limitations of the gradient furnace used, however, required the quenching of these wires after about 3 in. of crystal had been grown. As a result, an inch or so of each wire always was quenched from the gamma phase and retained a polycrystalline beta phase at room temperature. This polycrystalline beta was badly cracked. It was found that any attempt to deform it resulted in these cracks being propagated through the remaining uncracked crystals by a typical cleavage-type fracture.

The reason for this cracking is unknown, but, since all specimens of quenched beta contain excess chromium precipitated on the old gamma grain boundaries, it is possible that quenching strains initiate cracks in this harder phase. Attempts are being made to produce beta crystals from material of less than 1 atom % chromium.

DECLASSIFIED

TECHNICAL NOTES

TENTATIVE URANIUM-TITANIUM PHASE DIAGRAM

By A. U. Seybolt and D. W. White

Knolls Atomic Power Laboratory
General Electric Company
Schenectady, N. Y.

and F. W. Boulger and M. C. Udy

Battelle Memorial Institute
Columbus, Ohio

Report KAPL-470

The tentative phase diagram shown in Fig. 1 has been developed by thermal analysis, microscopic examination, dilatometric measurements, and x-ray diffraction. As is customary, the more uncertain features are shown dotted.

This work is the result of a rather rough survey in which highly pure metals were not used throughout. The main contaminant of importance was carbon, which ranged from 0.2 to 0.5 wt. % in all the alloys except those rich in uranium, wherein the carbon content was less than 0.1 wt. %. In plotting the phase diagram, corrections were applied to the titanium percentages by assuming the carbon to be present as TiC. Oxygen and nitrogen contents were not determined but may be high enough to have some effect on the diagram.

In spite of the use of somewhat impure metals, the major phase fields are believed to be described correctly on a semiquantitative basis, except perhaps certain portions of the uranium-rich end of the diagram.

Most of the alloys were arc-melted in an inert atmosphere using a water-cooled copper crucible, but some high in uranium were vacuum-melted in BeO crucibles using a high-frequency induction furnace. Alloys were made in 500- to 1000-g charges, depending upon the volume. Most of the alloys were forged and rolled at 1450 to 1800°F (790 to 980°C), although one or two compositions in the vicinity of the compound U_2Ti were too brittle to be readily fabricated at these temperatures.

The compound U_2Ti, which divides the diagram into two parts, is a stable high-melting phase of a hexagonal crystal structure, having three atoms per unit cell with $a_0 = 4.827$ A, $c_0 = 2.852$ A, $c/a = 0.591$ (see Report KAPL-309, pp. 24 to 26). A few optical pyrometer readings were taken of the melting point of an alloy very close to U_2Ti but with poor reproducibility. The best estimate of the melting point is about 2000°C (3630°F).

The region between the compound and 40 atom % titanium is in considerable doubt because no alloys in this composition range were examined. Impurity of the alloys makes the liquidus and solidus points above 40 atom % titanium uncertain. In fact, a gap of 100°C was found between the liquidus and solidus of the "100 per cent" titanium specimen. There is no doubt, however, that beta titanium dissolves a great deal of uranium and decomposes eutectoidally into U_2Ti and alpha titanium. On the other hand, solubility of uranium in alpha titanium is very limited. It appears to be between 0.3 and 1 atom % uranium.

On the uranium-rich end, some optical pyrometer readings of melting temperatures are spotted around the vicinity of the liquidus, but, owing to difficulties common to this type of observation, the scatter is high. The presence of the peritectic at 1200°C (2190°F) was shown primarily by thermal analyses and confirmed by typical reaction zones around the U_2Ti particles in the microstructure.

The extent of solid solubility of titanium in gamma uranium is in great doubt and may be considerably less or even greater than that indicated in the diagram. The region labeled "gamma uranium + U_2Ti" is also very much in question. Some spurious, but apparently very real, critical points obtained by thermal analyses (marked X) are difficult to interpret and

714 026

DECLASSIFIED

have been shown only as unconnected points in Fig. 1. They might possibly suggest a wide gamma-uranium solubility range, although, on the other hand, they may represent some entirely different behavior.

beta transformation for pure uranium. However, these temperatures are so close together that it is not certain whether a peritectoid or a eutectoid is involved. Nothing can be reported regarding the solubility of titanium in beta uranium and in alpha uranium as no alloys sufficiently low in titanium were studied.

The homogeneity range of the U_2Ti phase, at least on the uranium side, appears to be rather restricted.

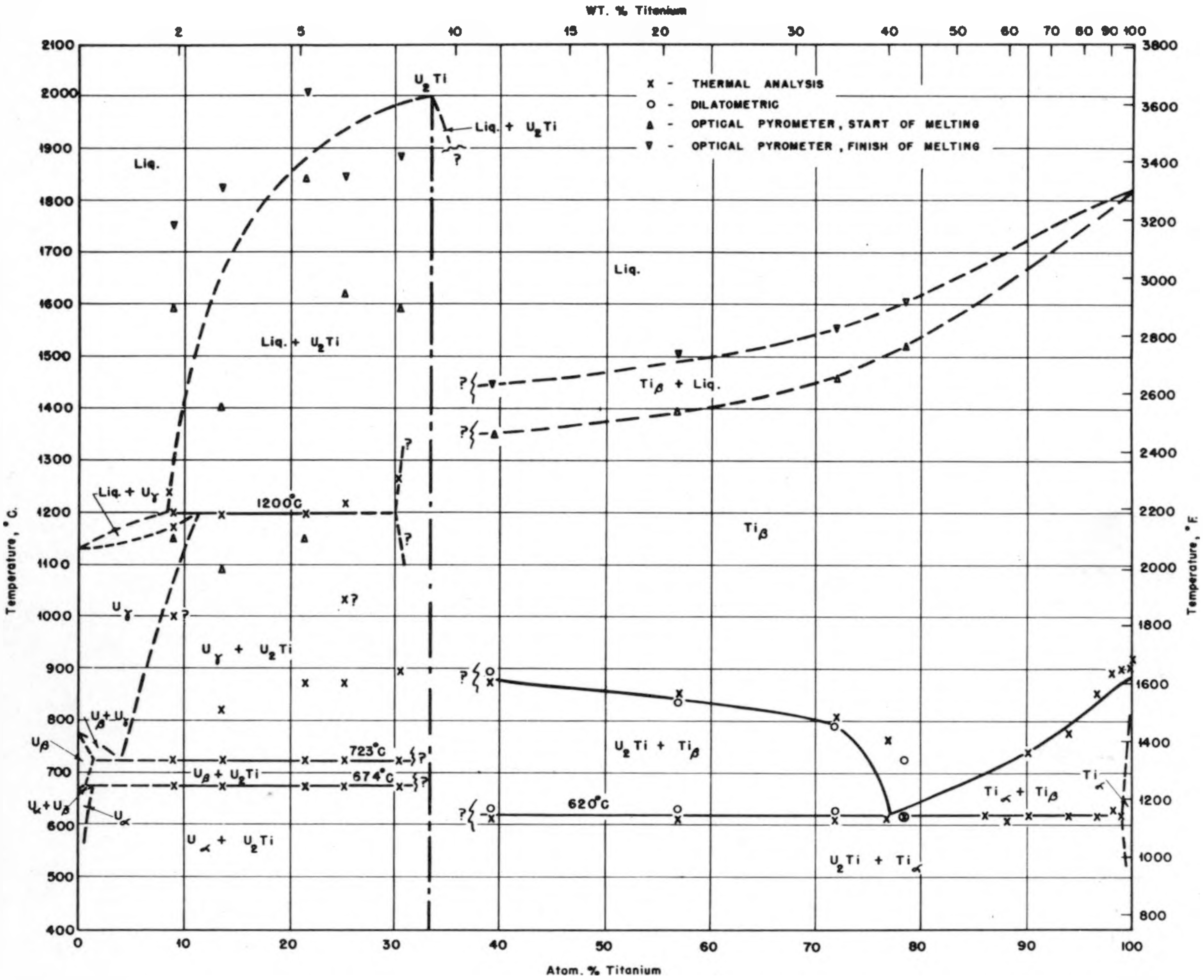


Fig. 1 — Tentative diagram for uranium-titanium sheet.

Gamma uranium decomposes eutectoidally into beta uranium and U_2Ti at 723°C (1330°F). Beta reverts to alpha at 674°C (1245°F) probably in a peritectoidal fashion, since the temperature of the reaction horizontal appears to be slightly higher than the alpha-

September 1950

227

TECHNICAL NOTES

Homopolar Generator Pump

By L. B. VANDENBURG

Knolls Atomic Power Laboratory
Schenectady, New York

Report TID-5004 (Del)

INTRODUCTION

A new type of electromagnetic pump combining a homopolar generator and a simple d-c pump into one unit promises high efficiencies and small size (see Fig. 1). The problems usually introduced by bearings, high temperatures, radioactivity, and bulky conversion equipment are largely eliminated.

HOMOPOLAR GENERATOR

A homopolar generator is simply a bar magnet with a concentric cylinder rotating around one end. The radial magnetic field is cut by the rotating cylindrical conductor, causing a voltage to appear axially along its length. If a cylindrical cup large enough to contain the rotor is built around one end of the magnet and is filled with liquid metal, the voltage will be transferred from the moving rotor to the stationary can.

HOMOPOLAR GENERATOR PUMP

The generator can be converted to a pump by adding a concentric pump channel around the outside of the can; the can is used as the inside wall, Fig. 2. The generated voltage is then short-circuited directly through the liquid metal to be pumped in the channel. The current reacts with the same magnetic field that created it, producing a force against the liquid metal which results in its moving in the same direction as the rotor.

PERFORMANCE

The performance of this pump is similar to an induction motor, Fig. 3. Letting ω_r equal the angular velocity of the rotor and ω_{lm} equal the angular velocity of the liquid metal, it can be shown that the theoretical efficiency and the hydraulic power output will be

$$\text{Efficiency} = \frac{\omega_{lm}}{\omega_r}$$

$$\text{Power} = K\omega_{lm}\,(\omega_r - \omega_{lm}) \quad \text{watts}$$

where

$$K = \frac{\beta_{lm}^2\, r_{lm}^2\, L^2 \times 10^{-16}}{R}$$

and

β_{lm} = gauss in liquid metal annulus
r_{lm} = radius of liquid metal channel
L = axial length of rotor
R = resistance of current path

LOSSES

The two major losses that subtract from the theoretical hydraulic power output, Fig. 3, are (1) the hydraulic loss from fluid friction and entrance-exit conditions and (2) the magnetic-drag loss due to end effects at the magnetic field boundary.

The hydraulic loss is proportional to ω_{lm}^3, and the magnetic-drag loss is proportional to ω_{lm}^2.

DECLASSIFIED

TII 228

PUMP CHARACTERISTICS

From Fig. 3 the following facts, which illustrate the potentialities of the pump, are deduced:

1. High efficiencies are available only at high ratios of ω_{lm}/ω_r.
2. The intersection of the loss and power curves determines the maximum flow and the maximum ratio of ω_{lm}/ω_r obtainable.
3. The hydraulic power output is equal to the length of the ordinate between the power and loss curve.
4. The intersection can be moved to the right by (1) reducing the losses or (2) increasing the power. Either practice results in a higher efficiency.

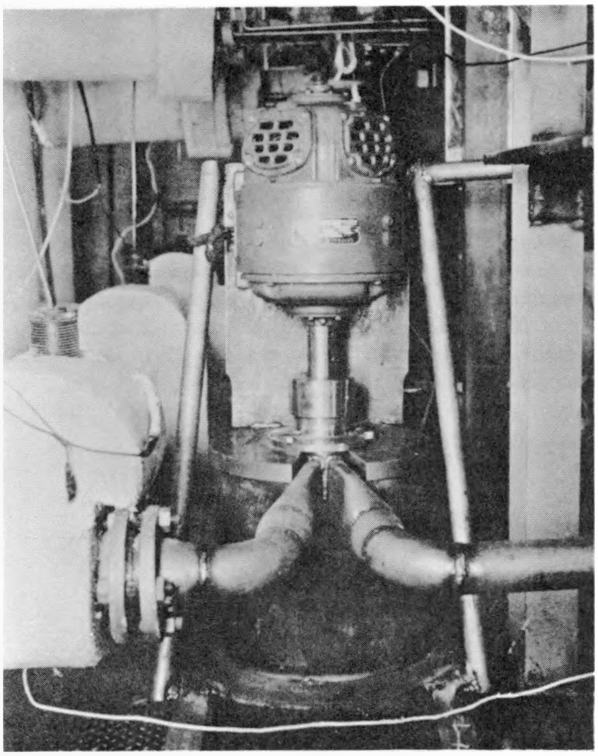


Fig. 1 — Homopolar pump generator.

DISCUSSION

The losses can be minimized by good pump design. It is evident from the power equation that the available power increases as the pump size increases. The losses will not increase accordingly. The resistance R should be kept to a minimum, being again a function of the design and material used in the pump. In general, any conducting liquid can be pumped by this means, providing it is not subject to electrolysis. The

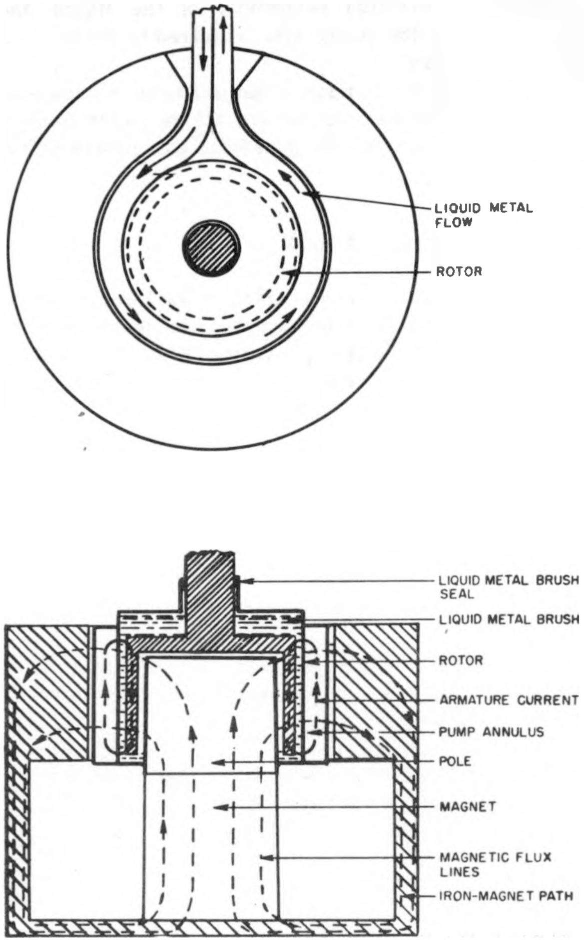


Fig. 2 — Simplified drawing of homopolar generator pump.

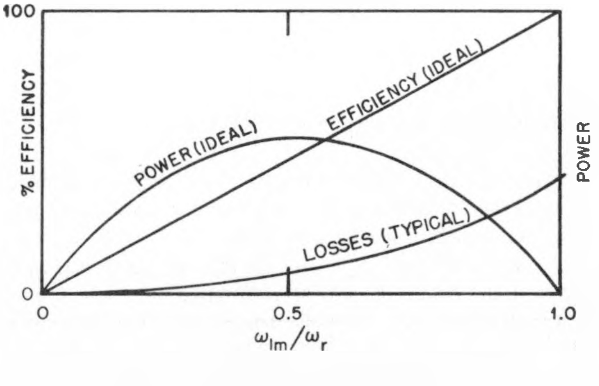


Fig. 3 — Graph of pump performance.

DECLASSIFIED

higher the electrical resistivity of the liquid, the larger will be the pump size required to maintain a given performance.

An increase in β^2 causes a proportional increase in the hydraulic power output and all the pump losses, with the exception of the hydraulic loss which is not affected.

EXPERIMENTAL RESULTS

The information in this article has been gathered from the study of a small experimental pump in which the losses were a large percentage of the output of the pump. The liquid metal used to test the pump was sodium, and NaK was used as a liquid brush for the armature circuit. The efficiency of this pump was 14 per cent. The maximum flow was 100 gal/min at 4.5 psi.

Extrapolation of these experimental results predicts efficiencies of 65 per cent at 30 psi for a 1500 gal/min pump with r equal to 15 in. and L equal to 12 in.

These figures are based on the use of a permanent magnet for a magnetomotive force source, and they allow for current leakage along the walls of the pump annulus.

April 1951

DECLASSIFIED

TECHNICAL NOTES

On the Removal of Na_2O from Na by Distillation

By LEO BREWER and JOHN L. MARGRAVE
Department of Chemistry and Radiation Laboratory
University of California, Berkeley, California

Report UCRL-1241 (Revised)

Lee[1] of the Mine Safety Appliances Co. has presented data indicating that in the atmospheric pressure distillation of Na (filtered at 150 to 175°C) the Na_2O passes off first, so that the still pot residue is leaner in oxygen than the initial feed or the distillate and the distillate uniformly contains 0.01 to 0.03 wt. % oxygen. Epstein and Weber[2] have considered this behavior on the basis of the simple solution laws, and they find (assuming that an unsaturated solution of Na_2O in Na follows Henry's law) that for an n plate distillation of a Na-Na_2O solution

$$W' = \left(\frac{Z}{W_S}\right)^n W$$

where W' = wt. % oxygen in the distillate
W = wt. % oxygen in the original sample
W_S = wt. % oxygen in saturated solution
Z = wt. % oxygen in vapor

Thus, for removal of oxygen from the still pot, W' must be greater than W or $\frac{Z}{W_S} > 1$.

Values for Z may be calculated, if the vapor pressures of Na and Na_2O are known, using Dalton's law. Epstein and Weber have used 13.7 mm Hg as the vapor pressure of Na_2O at the normal boiling point of Na (1187°K). Calculations by Brewer and Mastick[3] for the gaseous alkali metal oxides indicated that the vapor pressure of Na_2O at 1000°K is not over 5×10^{-7} atm and is due almost completely to decomposition to the gaseous elements. Bunzel and Kohlmeyer[4] have studied Na_2O at high temperatures, and they found its melting point to be 920°C. They state that at temperatures up to 1350°C practically no vaporization of Na_2O occurs. These data make it seem very unlikely that the vapor pressure of Na_2O is large enough to account for any vaporization from boiling Na.

A more plausible explanation for the removal of oxygen from the melt seems to be that arrived at by considering the carbon impurity present in the Na either as organic material or as Na_2CO_3. Available data indicate that at temperatures where the rate is appreciable, the reaction

$$Na_2CO_3 + 4Na = 3Na_2O + C$$

will occur. The free carbon available might then react as

$$Na_2O + C = 2Na(liq) + CO(gas)$$

The free-energy change and the equilibrium pressure of CO for this reaction have been calculated at four temperatures:

Temp., °K	ΔF, kcal	P_{CO}, atm
298	57.0	$10^{-41.8}$
500	46.2	$10^{-20.2}$
1000	19.5	$10^{-4.3}$
1187	10.5	$10^{-1.9}$

The low stability of Na_2C_2 makes its consideration of minor importance in these calculations.[5] On this basis the high equilibrium pressure of CO could well account for the removal of oxygen from the still pot and its transfer to the distillate in fractionations carried out at atmospheric pressure.

It seems very unlikely that Lee has actually observed fractional distillation of Na_2O from a Na-Na_2O solution. Our interpretation can easily be checked experimentally. Owing to the very endothermic nature of the reaction between Na_2O and C, the CO partial pressure will drop off rapidly with drop in temperature. Thus a low-pressure distillation should show little oxygen removal. Also our interpretation can easily be verified by distilling sodium containing an excess of oxide. After removal of the CO, it should not be possible to remove any more oxide from the still pot.

DECLASSIFIED

REFERENCES

1. R. C. Werner and C. B. Jackson, Mine Safety Appliances Co., Report on Research with Sodium and Sodium-Potassium Alloys from July 1, 1948, to May 31, 1949.
2. L. F. Epstein and C. E. Weber, J. Met. Ceram., 6: 80-82 (January 1951).
3. L. Brewer and D. Mastick, J. Am. Chem. Soc., 73: 2045 (1951).
4. E. Bunzel and E. Kohlmeyer, Z. anorg. Chem., 254: 1-30 (1947).
5. L. Brewer, L. A. Bromley, P. W. Gilles, and N. L. Lofgren, in "The Chemistry and Metallurgy of Miscellaneous Materials," National Nuclear Energy Series, Division IV, Volume 19B, Paper 4, McGraw-Hill Book Company, Inc., New York, 1950.

April 1951

TECHNICAL NOTES

Temperature Effect in D_2O-Uranium Lattices

By A. T. BIEHL and E. R. COHEN

Atomic Energy Research Department
North American Aviation, Inc.
Downey, California

Report TID-5029

The mean velocity of neutrons in a multiplying lattice is an important factor in the determination of a reactor behavior. E. P. Wigner[1] has pointed out that the effective temperature of the neutrons might be measured by comparing Eu_2O_3-foil activities with gold-foil activities since europium has approximately $1/v^2$ absorption and gold has $1/v$ absorption.

We have obtained an independent measurement of this effect by comparing, in an exponential experiment,[2] the flux distribution in similar multiplying and nonmultiplying lattices. The multiplying lattice consists of 1-in.-diameter uranium rods clad in 1-mm aluminum tubes. Nonmultiplying lattice is achieved by replacing the uranium with a lead-cadmium alloy whose absorption properties approximate uranium. A single 4-in.-long slug of uranium replaces one lead slug in the center of this lattice. Comparison of the flux distribution through the uranium and the moderator gives directly a comparison of the uranium cross section in the two lattices. Analysis of these measurements has indicated the absorption in the nonmultiplying lattice to be consistently higher than in the multiplying lattice and, hence, indicates that the neutrons have a lower mean velocity. These measurements have been performed with lattices of 4½ and 6 in. square cell spacing; no statistically significant difference between these two lattices was observed, although the mean neutron velocity should be lower in the wider spaced lattice. Expressed in terms of effective temperature, i.e., the temperature of a Maxwellian distribution with the same mean velocity, we find $\delta T/T = 0.11 \pm 0.08$ or $\delta T = 34 \pm 25$°C. (The quoted probable error has been increased by a factor of 2 over the statistical accuracy of the measurements to allow for uncertainties of method.)

These measurements have been checked, to a certain extent, through the use of europium foils which have been calibrated against gold foils in a thermal flux. The measurements, however, were made in a lattice of ¾-in. rods on a 6-in. square spacing and are, therefore, not exactly comparable to the other measurements. We find that the neutron temperature in the moderator is 5.3 ± 1.8% higher than in a purely thermal flux, while inside the uranium rods the temperature is 11.1 ± 1.6% higher. (The probable errors quoted are due mainly to the uncertainty of calibration of the europium foils.)

These results may be compared with an analysis of K. Cohen[3], who, on the basis of the velocity distribution of slowed down neutrons calculated by Wigner and Wilkins,[4] gives the following equation for the mean velocity in a homogeneous absorbing medium

$$\frac{\bar{v}}{\bar{v}_0} = 1 + 1.21 \frac{\sigma_a}{\xi \sigma_s}$$

We can adapt this formula to a heterogeneous lattice if we replace the cross sections by their mean values weighted by the approximate flux distributions in the lattice cell. Doing this for our experimental arrangement, we find $\delta T/T = 0.12$ for the 1-in. rods on 4.5-in. spacing and 0.06 for the 1-in. rods on 6-in. spacing. For the ¾-in. rods on 6-in. spacing, we have $\delta T/T = 0.035$. These numbers presumably refer to the average temperature throughout the lattice and therefore are more indicative of the temperature in the moderator than the temperature in the uranium where the strong absorption strongly perturbs the mean neutron velocity. The observed effect is in qualitative agreement with theory, but the accuracy of the present measurements is, however, too low to ascribe more than an order-of-magnitude significance to the results.

714 233

DECLASSIFIED

REFERENCES

1. Meeting of Reactor Physics Planning Group, April 9-10, 1951, Washington, D. C.
2. A. T. Biehl and E. R. Cohen, The NAA Exponential Experiment. I. Apparatus and Preliminary Procedure, Report NAA-SR-103 (in press).
3. K. Cohen, Low-enrichment Reactor for Naval Propulsion, Report HKF-102, Dec. 24, 1949.
4. E. P. Wigner and J. E. Wilkins, Jr., Effect of the Temperature of the Moderator on the Velocity Distribution of Neutrons . . ., Report AECD-2275, Sept. 13, 1948. (Original manuscript, Report CP-2156, Sept. 14, 1944.)

July 1951

234

DECLASSIFIED

TECHNICAL NOTES

Equilibrium in the Exchange of Deuterium Between Ammonia and Hydrogen (Part I)

By MORRIS PERLMAN, JACOB BIGELEISEN, and NORMAN ELLIOTT
Brookhaven National Laboratory

Report BNL-1007

INTRODUCTION

The equilibrium in the exchange reaction

$$NH_3 \text{ (gas)} + HD \text{ (gas)} \rightleftharpoons NH_2D \text{ (gas)} + H_2 \text{ (gas)} \qquad (1)$$

was studied above room temperature by Farkas,[1] Wirtz,[2] and Herrick and Sabi.[3] The recent experiments of Claeys, Dayton, and Wilmarth[4] show that this reaction in the liquid is fairly rapid when catalyzed by KNH_2. The work reported here was undertaken to obtain equilibrium data at, and below, room temperature.

EXPERIMENTAL METHOD

Equilibration

The apparatus in which the equilibration of ammonia and hydrogen was allowed to take place is shown in Fig. 1. Measurements were made at temperatures below the normal boiling point of ammonia with liquid ammonia and at room temperature with ammonia gas. In all experiments the gas equilibrium was measured.

For the low-temperature experiments 18.5 ml of liquid ammonia containing approximately 5 at. % deuterium was condensed onto approximately 1 g of KNH in vessel A. The preparations of these materials are described below. Constant temperature was maintained in the system by a bath of melting solid held in the Dewar vessel B; the temperature was measured with a calibrated copper-constantan thermocouple and was constant to better than 0.1°C. A tank H_2-HD mixture approximately 5 at. % D, released from UH_3-UH_2D, was metered into the calibrated bulb C to a pressure of 25 cm Hg. It was then transferred into vessel A by application of gas pressure to the mercury reservoir. The rotating inverted cone, driven by a shaft passing through a Wilson seal, served to lift the solution continuously and to throw it out as a spray. The liquid pumping rate was approximately 10 ml/sec. The gas phase was circulated by the motion of the fan blades. At intervals small gas samples for isotopic analysis were withdrawn into the side-arm volumes at D and E. It was demonstrated that the time for complete gas mixing in vessel A was less than 15 sec. The reaction was allowed to continue until the isotopic composition of the components of the gas samples became constant. In a separate experiment it was found that the half time for the exchange of deuterium between the amide catalyst and liquid ammonia was short compared with the equilibration times.

DECLASSIFIED

For the room-temperature measurements gaseous ammonia and hydrogen were metered into vessel A, which contained a small quantity of a commercial solid catalyst, either platinized charcoal or a mixture of supported nickel and ruthenium. In all other respects the procedure was the same as that used for the low-temperature measurements.

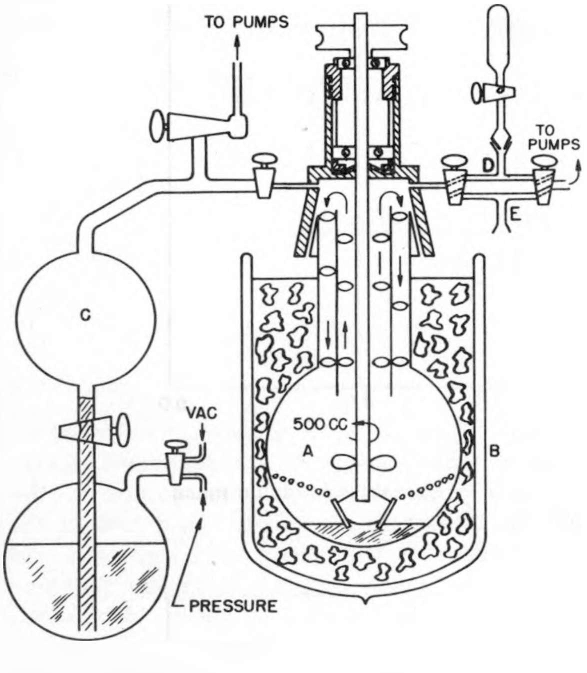


Fig. 1—Equilibration apparatus for ammonia and hydrogen.

The gas samples for analysis were pumped through a trap cooled by liquid nitrogen to separate the hydrogen from the ammonia.

Analysis

For deuterium analyses all samples were in the form of hydrogen gas. Conversion of the ammonia was effected by reaction with cleaned uranium-metal turnings at a temperature of about 475°C in accord with the equation

$$xNH_3 + U \rightleftharpoons UN_x + \tfrac{3}{2}xH_2 \qquad (2)$$

The conversion was carried out in the apparatus shown in Fig. 2, which was designed to permit repassage of any small amounts of unreacted ammonia over the hot metal. The recovery of hydrogen from the decomposition of ammonia was quantitative; sensitivity tests demonstrated the absence of memory. Identical results were obtained from the uranium reaction and from the reaction with magnesium at 600°C, which is much less conveniently carried out.

The isotopic analyses were performed with a General Electric Company mass spectrometer by comparison with standards. A glass pinhole leak was installed in the instrument. Corrections amounting to about 0.15 per cent of the H_2^+ peak height were made for the H_3^+ ion.

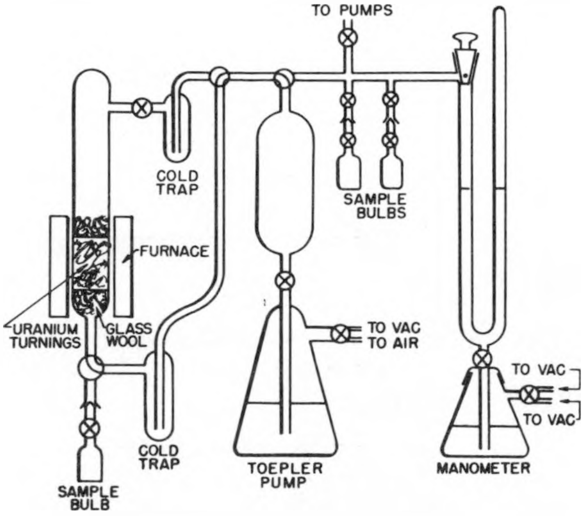


Fig. 2—Apparatus for the conversion of NH_3 to H_2.

Ten HD-H_2 mass-spectrometer calibration mixtures in the range 0.5 to 5.0 at.% deuterium were prepared by the quantitative reduction of standard water samples, gravimetrically synthesized, over powdered zinc metal at 400°C. Memory effects were found to be absent, but as a precautionary measure the apparatus was swept prior to each preparation with small samples of water of the preparation composition. A typical calibration curve is shown in Fig. 3.

PREPARATION OF MATERIALS

Ammonia containing about 5 at. % deuterium was prepared by the addition of NaOH and

0317122A1030

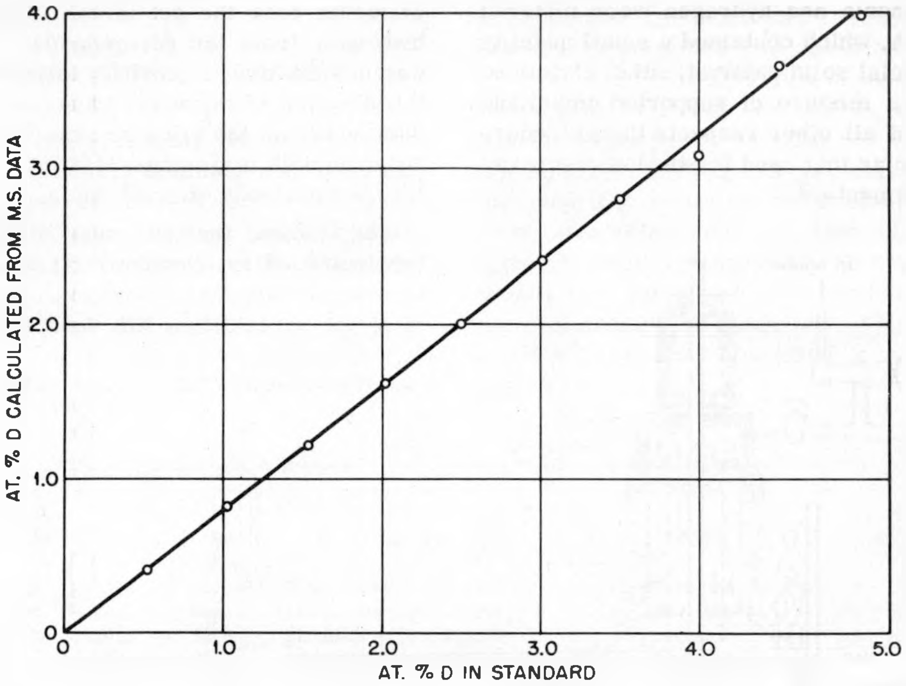


Fig. 3—Atom % deuterium in standard vs. at. % deuterium calculated from mass spectrometer data.

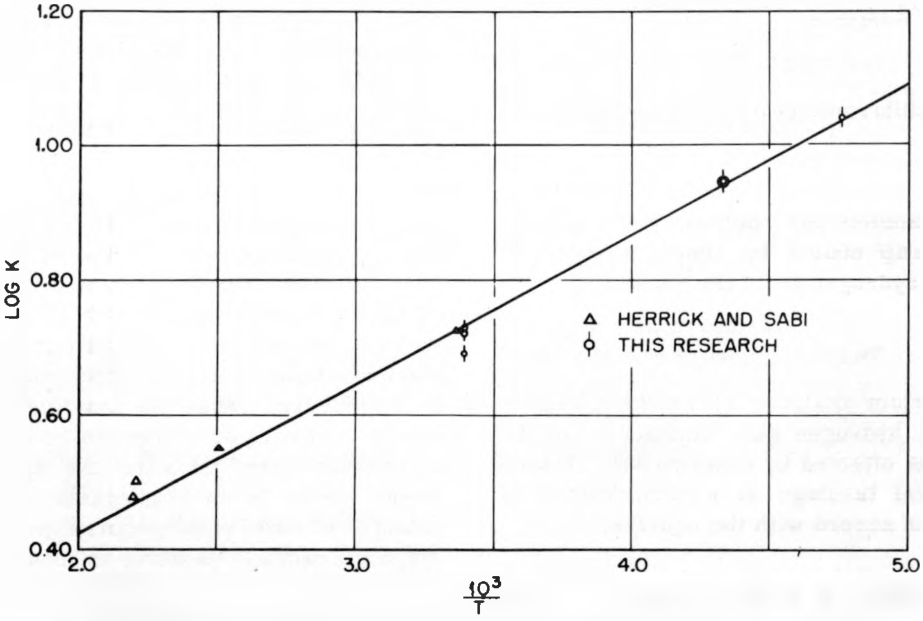


Fig. 4—Equilibrium constant for the reaction HD (gas) + NH_3 (gas) $\rightleftharpoons$ H_2 (gas) + NH_2D (gas) as a function of temperature.

714 237

DECLASSIFIED

NH_4NO_3 to an excess of 5 per cent D_2O-95 per cent H_2O mixture. The ammonia was dried by means of cold traps and sodium metal; it was stored as liquid in a nickel cylinder.

Potassium amide was prepared in a nickel apparatus by the passage of ammonia through liquid potassium at 350°C. The reaction was judged complete when no more hydrogen was present in the exit gas. The amide was stored in closed containers and showed little deterioration on standing. This material was easily handled in air, in contrast to the potassium amide prepared by a catalyzed reaction in liquid ammonia.

For the ammonia gas

$$D_N = \frac{NH_2D + 2NHD_2 + 3ND_3}{3(NH_3 + NH_2D + NHD_2 + ND_3)} \qquad (6)$$

where D_N is the atom fraction of deuterium in the hydrogen obtained from the ammonia. Because the atom fraction of deuterium did not exceed 0.05, the ND_3 concentration may be neglected. It is assumed that for the reaction

$$NHD_2 + NH_3 \rightleftharpoons 2NH_2D \qquad (7)$$

the distribution of deuterium is random, $K_7 = 3$.

Table 1—Equilibrium in the Reaction NH_3 (gas) + HD (gas) $\rightleftharpoons$ NH_2D (gas) + H_2 (gas)

Expt. No.	T,°K	Catalyst	Approach	D_h ± av. dev.	D_N ± av. dev.	$\frac{HD}{H_2}$ (gas)	$\frac{NH_2D}{NH_3}$ (gas)	K_1
5	295	Ni + Ru	5 at. % NH_3-D; H_2	0.0108 ± 0.0002	0.0367 ± 0.0004	0.0218	0.115	5.26 ± 0.1
8	295	Pt	6 at. % H_2-D; NH_3	0.0091 ± 0.0000	0.0318 ± 0.0003	0.0184	0.0988	5.37 ± 0.1
6	295	Ni + Ru	5 at. % NH_3-D; H_2	0.0122 ± 0.0001	0.0384 ± 0.0002	0.0247	0.121	4.92 ± 0.1
1	231	KNH_2	5 at. % NH_3-D; 5 at. % H_2-D	0.0091 ± 0.0001	0.0509 ± 0.0007	0.0184	0.163*	8.86 ± 0.2
3	231	KNH_2	5 at. % NH_3-D; 0.7 at. % H_2-D	0.0091		0.0184		
2	210	KNH_2	5 at. % NH_3-D; 1 at. % H_2-D	0.0072 ± 0.0002	0.0513 ± 0.0012	0.0145	0.161*	11.1 ± 0.2

*These values were obtained by use of the smoothing procedure discussed in the text.

Results

From the analytical data the HD/H_2 and NH_2D/NH_3 ratios for the gaseous equilibrium were calculated in the following manner:

For the hydrogen gas

$$D_h = \frac{HD + 2D_2}{2(H_2 + HD + D_2)} \qquad (3)$$

where D_h is the atom fraction of deuterium and the other symbols are numbers or concentrations of the particular species. Adequate correction for the small amounts of D_2 present in these experiments may be made with the assumption that for the reaction

$$H_2 + D_2 \rightleftharpoons 2HD \qquad (4)$$

the equilibrium constant is 4. It follows that

$$\frac{HD}{H_2} = \frac{2D_h}{1 - D_h} \qquad (5)$$

This assumption is supported by the fact that the distribution of deuterium and protium is close to random in disproportionation reactions, except in the case of reaction 4. For example in the reaction

$$H_2O + D_2O \rightleftharpoons 2HDO \qquad (8)$$

at 200°K, $K_8 = 3.86$.*

It follows that

$$\frac{NH_2D}{NH_3} = \frac{3D_N}{1 - 3D_N + (2 - 3D_N)D_N/(1 - D_N)} \qquad (9)$$

Results are summarized in Table 1.

In experiments 1, 2, and 3 the isotopic composition of the liquid was constant. Although the NH_2D (gas)/NH_3 (gas) ratios in these experiments could have been used with sufficient accuracy directly as calculated from the deuterium

---

*Unpublished calculations based on the potential function of B. T. Darling and D. M. Dennison.[5]

714 238

DECLASSIFIED

analyses, the logarithms of the ratios thus obtained were plotted against 1/T; an additional ratio was obtained from this liquid at room temperature. Through the three points a line was drawn whose slope corresponded to the proper change of vapor pressure ratio with temperature.[6] The desired NH_2D (gas)/NH_3 (gas) values were read from this line.

In experiments 5 and 6 a calculation of the material balance showed that an over-all dilution of the deuterium by protium had occurred. The fact that no dilution was observed in experiment 8, in which the quantity of catalyst was reduced about 100-fold, demonstrates that this dilution arose from an adsorbed layer, probably water, on the catalyst.

Figure 4 shows the values of log K plotted against 1/T. The results of Herrick and Sabi are included. In the temperature range 200 to 500°K the data may be represented by an equation of the form

$$\ln K_1 = A + (B/T) \tag{10}$$

in accord with theoretical expectations; at higher temperatures, however, K_1 must approach 3/2 asymptotically. A value for A was calculated theoretically by the method of Bigeleisen and Mayer[7] from the ratio of the classical frequencies[8] of H_2 and HD, from the masses and moments of inertia of NH_3 and NH_2D, and from the symmetry numbers. The products of the moments of inertia were calculated[9] from the internuclear distances.[10] The curve in Fig. 4 was drawn through the calculated point at 1/T = 0 (ln K = A) and the experimental points of this work. In Eq. 10 A = −0.046; the value of B, derived from the slope of the line, is 512°K.

Zero-point-energy Calculation

The vibrational spectrum of ammonia has not been analyzed sufficiently well to permit the calculation of its zero-point energy.[11] From the value of B in Eq. 10, from the difference in the zero-point energies of H_2 and HD, and from the rotational constants of H_2 and HD, the difference in the zero-point energies of NH_3 and NH_2D may be calculated.[7] The relation is

$$\frac{E^\circ_{0\,NH_3} - E^\circ_{0\,NH_2D}}{k} = B + \frac{(E^\circ_{0\,H_2} - E^\circ_{0\,HD})}{k} + \frac{(\sigma_{HD} - \sigma_{H_2})T}{3} \tag{11}$$

where k is the Boltzmann constant. The zero-point energies and values of σ for H_2 and HD were calculated from the data of Herzberg.[12] The value obtained for $(E^\circ_{0\,NH_3} - E^\circ_{0\,NH_2D})/k$ is 916 ± 5°, which is equivalent to $(E^\circ_{0\,NH_3} - E^\circ_{0\,NH_2D})/hc = 637 \pm 3\ cm^{-1}$.

ACKNOWLEDGMENTS

We wish to thank A. P. Irsa for carrying out the analyses with the mass spectrometer and H. C. Prosser for his help in the preparation of standards and materials.

REFERENCES

1. A. Farkas, Trans. Faraday Soc., 32: 416 (1936).
2. K. Wirtz, Z. physik. Chem., B30: 289 (1935).
3. C. E. Herrick, Jr., and N. Sabi, Columbia University Report A-765, July 30, 1943.
4. Y. Claeys, J. Dayton, and W. K. Wilmarth, J. Chem. Phys., 18: 759 (1950).
5. B. T. Darling and D. M. Dennison, Phys. Rev., 57: 128 (1940).
6. I. Kirshenbaum and H. C. Urey, J. Chem. Phys., 10: 706 (1942).
7. J. Bigeleisen and M. G. Mayer, J. Chem. Phys., 15: 261 (1947).
8. G. Herzberg, "Molecular Spectra and Molecular Structure (I)," p. 141, Prentice-Hall, Inc., New York, 1939.
9. J. O. Hirshfelder, J. Chem. Phys., 8: 431 (1940).
10. M. V. Migeotte and E. F. Barker, Phys. Rev., 50: 418 (1936).
11. G. Herzberg, "Infrared and Raman Spectra of Polyatomic Molecules," p. 294, D. Van Nostrand Company, Inc., New York, 1945.
12. G. Herzberg, "Molecular Spectra and Molecular Structure (I)," p. 487, Prentice-Hall, Inc., New York, 1939.

DECLASSIFIED

TECHNICAL NOTES

A Technique for Producing Fine-particle Thorium Oxide and Uranium Oxide

By ROBERT S. HANSEN and ROBERT E. MINTURN

Ames Laboratory, Institute for Atomic Research,
Iowa State College, Ames, Iowa

Report ISC-145

Current interest in the development of homogeneous reactors has led to a corresponding interest in the development of stable slurries of uranium-containing compounds. A parallel interest in slurries of thorium-containing compounds also exists.

In view of contemplated pumping operations, low-viscosity slurries would be of special value. On the other hand, while the operation of a homogeneous reactor would tend to maintain a slurry suspended by strong agitation, a reasonable stability at rest would be desirable in the event of temporary shutdowns. These considerations suggest an approach to the slurry problem through preparation of ultrafine particles of the material to be dispersed and subsequent dispersion of the material in the desired solvent using a colloid mill and suitable stabilizing agents.

It has been found possible and practical to prepare such ultrafine particles of uranium oxide and thorium oxide by the combustion of atomized solutions of the corresponding nitrates in suitable organic solvents.

In the preparation of uranium oxide a solution of uranyl nitrate in acetone containing 125 g of $UO_2(NO_3)_2 \cdot 9H_2O$ per liter of acetone was used as feed for the spray-burner system. Thorium nitrate does not form a stable solution in acetone, but a suitable feed material could be prepared by adding to 100 g of $Th(NO_3)_4 \cdot 4H_2O$, first, 150 ml of ethanol and heating until a substantially clear solution is obtained (about 1 hr); the resulting solution is then diluted by the addition of 1 liter of acetone. In the latter preparation the resulting solution was not entirely clear; insoluble material was allowed to settle out, and the clear supernatant liquid was used for spray-burner feed.

The spray-burner system is illustrated in Fig. 1. The fuel, prepared as indicated previously, was stored in a 5-gal carboy. This reservoir was connected by glass and Tygon tubing to an 8-in. test tube in a manner that provided automatically a level of feed solution in the test tube above any desired minimum. The air supply was a standard laboratory pressure line and was connected by pressure tubing to the spray burner as illustrated, the air-blast nozzle being a 2-mm-I.D. capillary drawn to about 0.7 mm I.D. at the tip. The fuel-intake capillary was 0.5-mm-I.D. capillary tubing. A fuel drain, coupled to a closed flask, was provided for undrained liquid, and an air bleed permitted adjustment of air-flow rate. The burner nozzle was 20-mm-I.D. Vycor tubing. In the production of uranium oxide smokes, using feed solutions of the concentration indicated, it was necessary to place a 20-mesh platinum screen over the nozzle mouth to decrease turbulence and ensure sustained burning; the screen became red hot and tended to clog after several hours of operation. Reduction of the uranyl nitrate concentration by about 20 per cent permitted elimination of the screen,

TIA 240
18

DECLASSIFIED

and no screen was needed for thorium nitrate solutions of the concentration indicated. Without the screen the burner appeared suitable for prolonged operation and has been operated continuously for 10 hr. The collecting tube was a 6-ft refractory-lined stove pipe 6 in. in diameter.

To begin operation, the air-supply valve was opened, the air bleed was opened wide, a match was held to the end of the burner nozzle, and the air-bleed valve was adjusted until the flame burned evenly at the tip of the nozzle. After the burner nozzle became hot, it was necessary to increase the opening of the air-bleed valve slightly. The whole system was inclined at about 10 deg from horizontal to permit drainage of the burner nozzle to the fuel drainback and to give a slight chimney effect to the collecting tube.

On completion of a run the collecting tube was allowed to cool, and the deposited smoke was scraped off with a rubber policeman. The resulting powder was washed first with water and then with acetone and was dried at 110°C. With the collection method used, the yield was 25 per cent of theoretical maximum.

Figures 2 and 3 are electron microphotographs of uranium oxide and thorium oxide particles, respectively, produced in this manner. An x-ray powder photograph of the uranium oxide indicated it to be about 70 per cent U_2O_5.[1,2] Surface areas of the powders were determined by nitrogen adsorption, according to the Brunauer-Emmett-Teller method.[3] The surface area of the uranium oxide was found to be 12 m^2/g (particle diameter 60 $m\mu$), that of thorium oxide 16.6 m^2/g (particle diameter 38 $m\mu$).

A study of slurries of these oxides is in progress and will be reported in the near future.

The authors are indebted to Dr. P. H. Carr for the electron microphotographs, to W. V. Fackler, Jr., for surface-area determinations, and to Ralph Hach for the x-ray powder analysis of the uranium oxide.

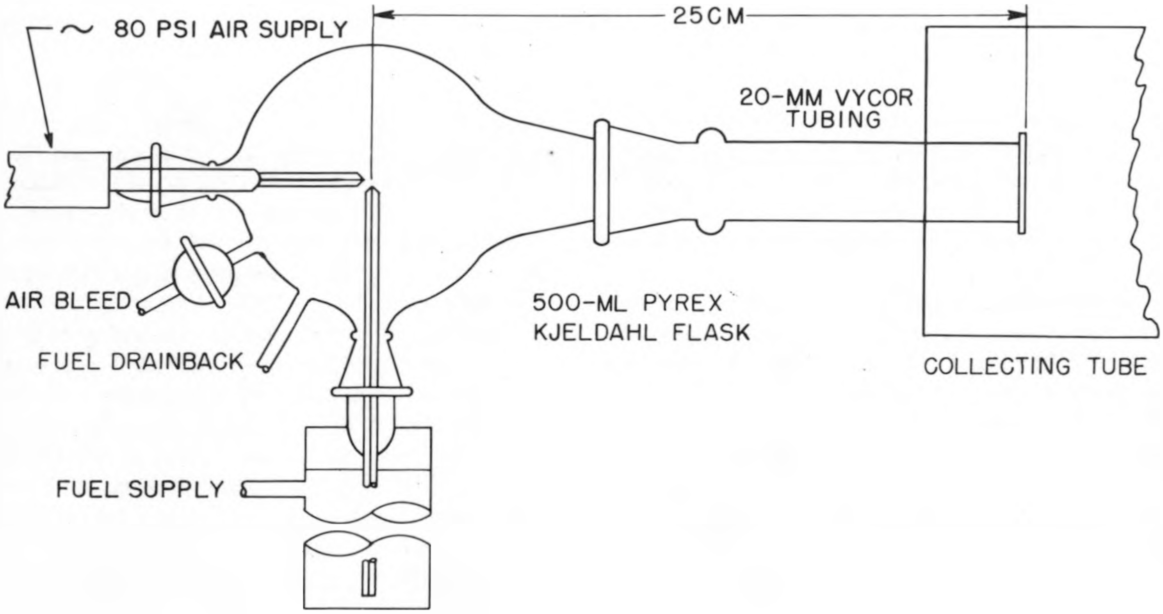


Fig. 1—Atomizer and burner.

REFERENCES

1. R. E. Rundle, N. C. Baenziger, A. S. Wilson, and R. A. McDonald, A Summary of X-Ray Information on Hydrides, Deuterides, Carbides, Nitrides, and Oxides of Uranium, Report CC-2397, Feb. 17, 1945.
2. N. C. Baenziger, The Crystal Structures of Some Thorium and Uranium Compounds, Report ISC-99, Oct. 15, 1948.
3. S. Brunauer, P. H. Emmett, and E. Teller, J. Am. Chem. Soc., 60: 309 (1938).

TID 241
19

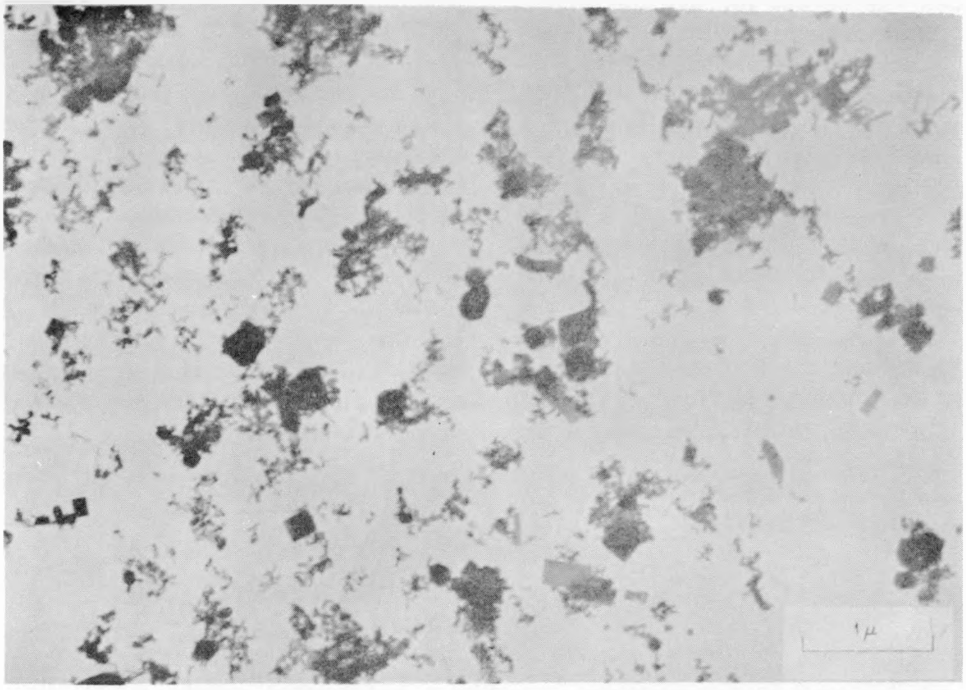


Fig. 2—Microphotograph of uranium oxide particles.

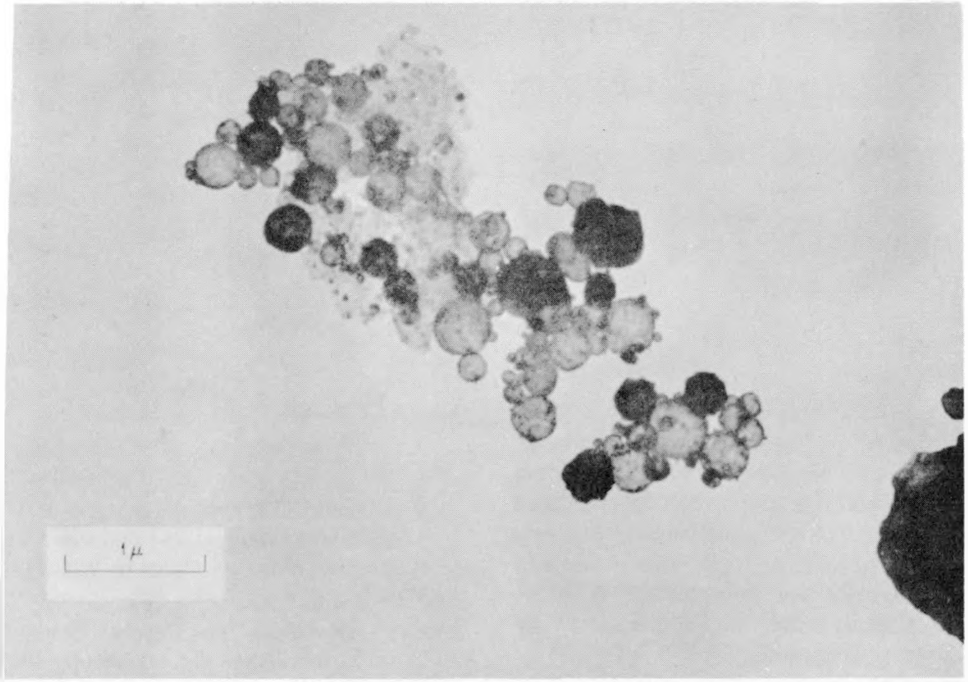


Fig. 3—Microphotograph of thorium oxide particles.

DECLASSIFIED

TECHNICAL NOTES

The Vanadium-Uranium Constitutional Diagram

By H. A. SALLER and F. A. ROUGH
Battelle Memorial Institute

Report BMI-HAS-4

INTRODUCTION

Vanadium has a low capture cross section for fast neutrons. This condition brought about interest in its use as a diluent or as a structural material for fast power breeders. The metal would presumably be used in connection with uranium or as a uranium alloy. It was for this reason that knowledge of the vanadium-uranium constitutional diagram was considered important and studies of the diagram were instituted. The diagram developed is considered adequate, and no further work on it is contemplated.

PREPARATION AND METHODS OF STUDY

The first studies were made on alloys prepared from calcium-reduced vanadium, produced at Knolls Atomic Power Laboratory, and good Mallinckrodt biscuit uranium: To check these studies, alloys were produced from iodide vanadium of high purity and good biscuit uranium. Experiments performed on these alloys produced only minor revisions of the diagram.

Alloy ingots up to 30 at. % vanadium were prepared by melting in beryllia crucibles. Spectrographic analyses of these alloys showed no appreciable contamination from melting. The remainder of the alloys were prepared by arc-melting techniques.

The principal studies of the alloys were made by metallographic and thermal analyses. X-ray diffraction was utilized to verify some of the results of early metallographic studies.

Thermal analyses were performed using a differential thermocouple to detect transformations.[1] Metallographic methods of examination were varied with the compositions of the alloys being studied.

RESULTS

The results of combined studies are shown in Fig. 1. Supporting data obtained by metallographic and thermal analyses are plotted in the diagram. No intermetallic compounds occur in the system. Additions of vanadium lower the melting point of uranium, forming a eutectic reaction at 18 at. % vanadium and 1040 ± 5°C. The solubility of vanadium in gamma uranium decreases from 12 per cent at the eutectic temperature to 9 per cent at the eutectoid temperature, 727 ± 5°C, where the gamma transforms to beta uranium and vanadium (delta phase).

The solubility of vanadium in beta uranium is considerably less than in the gamma, being about 2 at. % at 700°C. Quenching of 2 per cent alloys from the beta range retained the beta phase and produced some microcracking. Cracking was not observed in alloys containing considerable quantities of vanadium as a second phase.

The alpha-uranium solubility is less than the beta, being about 1.5 per cent vanadium at 600°C.

Uranium is soluble in vanadium up to 4 at. % (15 wt. %). The solubility decreases slightly with decreasing temperature.

REFERENCE

1. National Bureau of Standards, Technical Paper 170, 1921.

August 1951

243

DECLASSIFIED

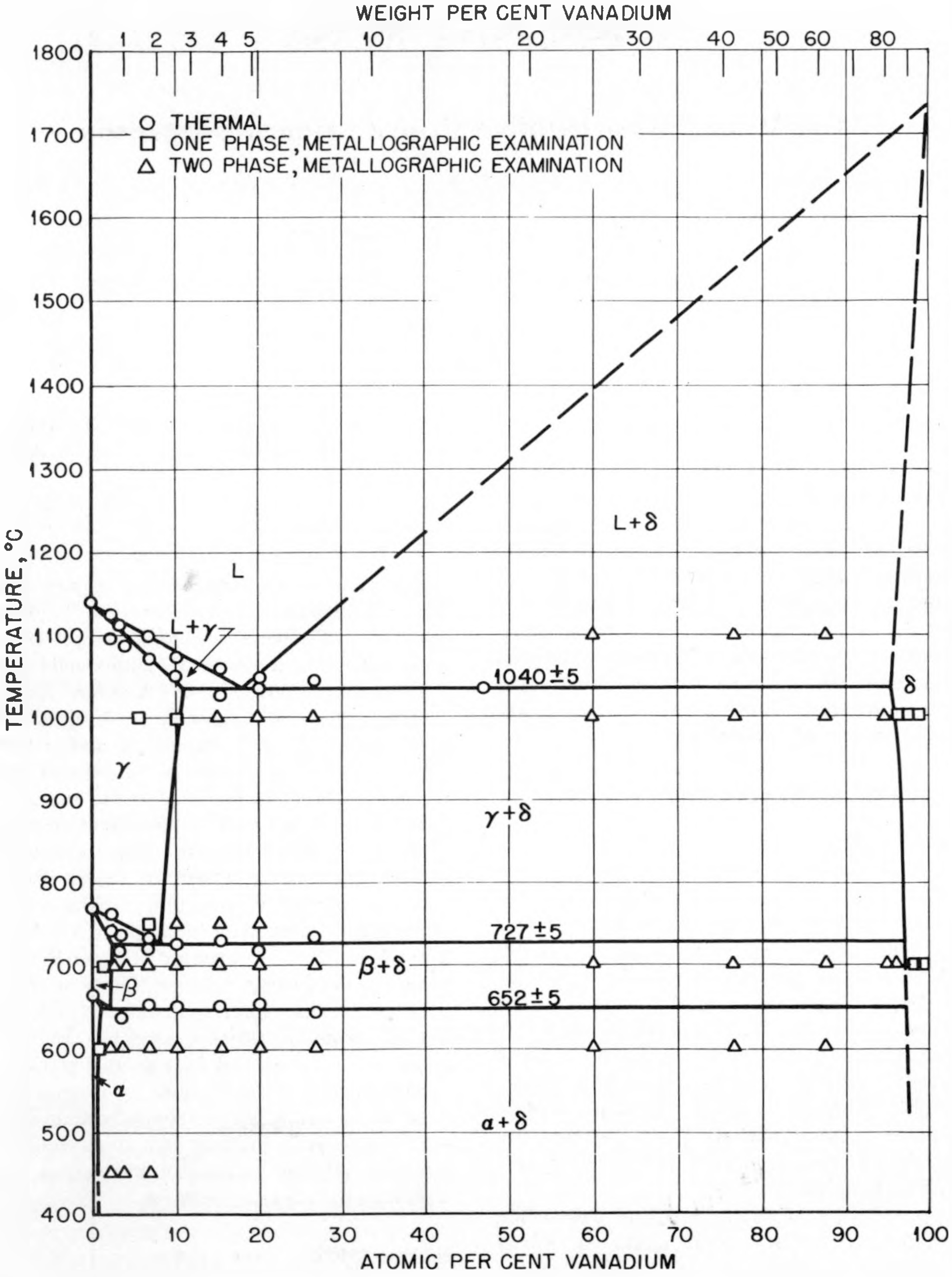


Fig. 1 — Vanadium-uranium constitutional diagram.

2/4
22

TECHNICAL NOTES

Anodic and Cathodic Treatment of Type 347 Stainless Steel During Passivation with Nitric Acid or Chromic Acid Solutions

By M. H. LIETZKE

Oak Ridge National Laboratory

Report CF-51-10-141

INTRODUCTION

The type 347 stainless steel to be used in the Homogeneous Reactor Experiment can be passivated by heating in either 1 per cent HNO or 2 per cent CrO_3 solution at 250°C for 24 hr. Since either treatment is believed to produce a passive oxide film on the surface of the steel, it seemed of interest to determine whether anodic treatment of the steel during either of the passivation processes might not produce a superior passive film. Cathodic treatment during passivation was also investigated.

EXPERIMENTAL METHODS

Specimens of type 347 stainless steel freshly passivated in either the HNO_3 or CrO_3 solutions showed a potential greater than 700 mv more positive than the saturated calomel electrode when immersed in a 0.13-*f* UO_2SO_4 solution (corresponding to 30 g of uranium per liter). The potential became somewhat less positive when the passivated steel specimen was maintained at 100°C in the UO_2SO_4 solution under reflux conditions. As long as the film was intact, the curve obtained by plotting potential vs. time did not show any sudden breaks. However, if sufficient KCl was added to the UO_2SO_4 solution, the potential of the passivated steel with respect to the saturated calomel electrode might suddenly become much less positive, indicating failure of the passive film. The length of time before sudden breaks were observed in the potential-vs.-time curve, when the uranyl sulfate solution at 100°C was made 0.2M in KCl, was taken as a measure of the quality of the passive film being studied. The potential was measured by a vibrating-reed electrometer and was recorded by a Brown recording potentiometer.

In all the experiments specimens of stainless steel wire were used. During passivation the pieces of wire were inserted through a soapstone fitting into an American Instrument Co. bomb and hence were insulated from the bomb proper. In the experiments involving anodic or cathodic treatment of the steel during passivation the specimen served as either anode or cathode and the bomb itself as the other electrode. Current for the anodic or cathodic treatment was supplied by means of a lead storage battery.

EXPERIMENTAL RESULTS

Conditioning the Film

It was observed in the first experiments that HNO_3-passivated specimens failed almost immediately when placed directly in a uranyl sulfate solution that was 0.2M in KCl. However, the passive films appeared much more resistant to the Cl^- when they were maintained in contact with the UO_2SO_4 solution at 100°C for 48 hr prior to the addition of the KCl. Hence all specimens used in subsequent experiments were

2-3

714 245

DECLASSIFIED

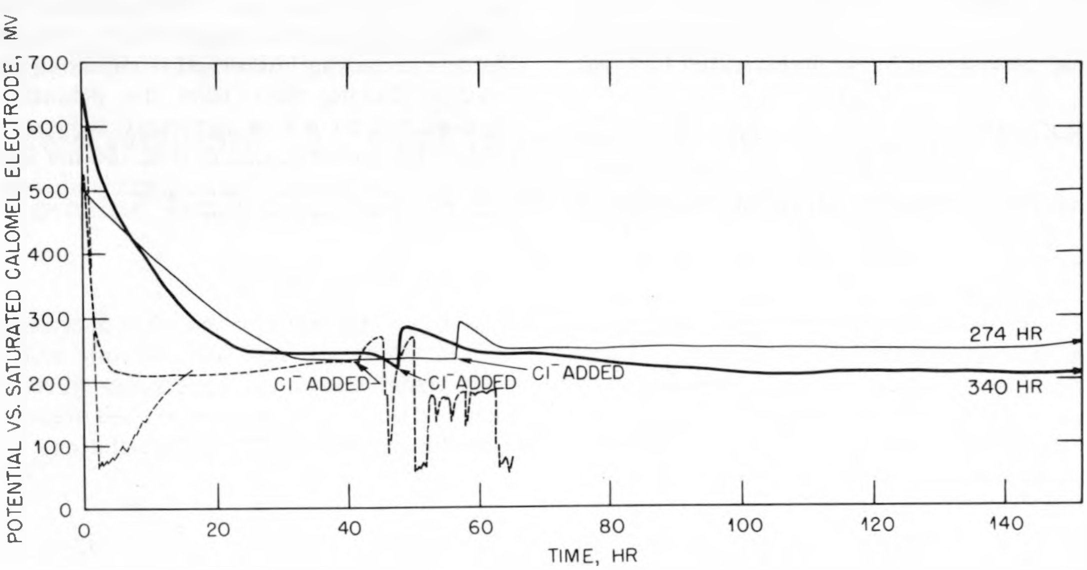


Fig. 1—Effect of anodic treatment of type 347 stainless steel at various current densities during passivation in 1 per cent HNO$_3$.——, no anodic treatment.——, anodic treatment at 0.0021 amp/sq ft.----, anodic treatment at 0.021 amp/sq ft. ----, no anodic treatment, no conditioning in UO$_2$SO$_4$ solution.

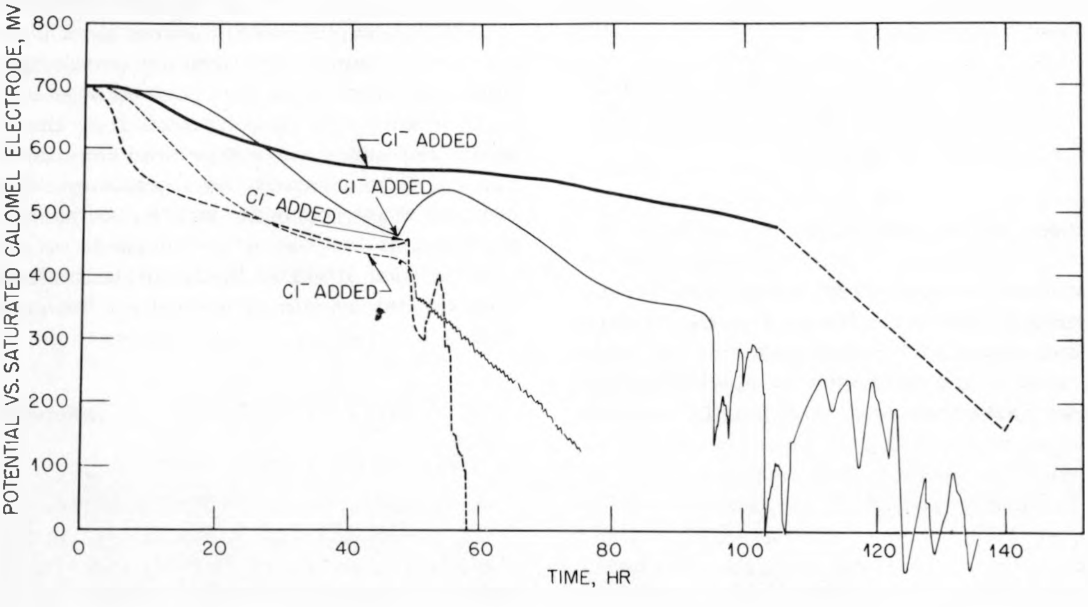


Fig. 2—Effect of anodic treatment of type 347 stainless steel at various current densities during passivation in 2 per cent CrO$_3$ solution.——, no anodic treatment.——, anodic treatment at 0.0021 amp/sq ft. ----, anodic treatment at 0.021 amp/sq ft.----, anodic treatment at 0.21 amp/sq ft.

714 246

DECLASSIFIED

subjected to this preliminary treatment before KCl was added to the solution. The actual changes that occur in the film during this conditioning period are being investigated further.

Nitrate Passivation

Figure 1 shows the potential-vs.-time curves obtained with specimens of nitrate-passivated type 347 stainless steel. The initial decrease in potential probably corresponded to the removal of oxygen from the passive film. When the Cl^- was added (as KCl dissolved in a small amount of UO_2SO_4 solution), some oxygen was also introduced into the system, which caused the sudden humps in the curve. As far as the curves were followed after the addition of the KCl, no breaks were observed in the case of the specimens given no anodic treatment or anodized at 0.0021 amp/sq ft during passivation. However, these specimens failed immediately if they were not conditioned in the UO_2SO_4 solution before the addition of the chloride. The specimen given anodic treatment at 0.021 amp/sq ft failed 3 hr after the addition of the KCl even though it was previously conditioned in the UO_2SO_4 solution.

Chromate Passivation

Figure 2 shows the effect of anodic treatment of 347 stainless steel at various current densities during passivation in 2 per cent CrO_3 solution. The specimen that received no anodic treatment lasted for over 62 hr before it failed. The length of time the anodized specimens remained good decreased with increasing anodic current density during passivation. Hence it appears from these experiments that the passive film produced on 347 stainless steel anodized in 2 per cent CrO_3 at 250°C is inferior to that produced under the same conditions but without anodic treatment. The potential of a specimen passivated in 2 per cent CrO_3 solution without anodic treatment was followed for 426 hr while the specimen was immersed in refluxing UO_2SO_4 solution. During this time the potential decreased to +80 mv vs. saturated calomel electrode. The potential dropped to +80 mv in about 300 hr, and then maintained this value for the duration of the experiment.

Cathodic Treatment

Cathodic treatment of the steel was also tried in both the nitric acid and chromic acid solutions. Even though the specimens were conditioned in UO_2SO_4 solution they failed immediately upon the addition of KCl to the solution.

CONCLUSION

From these experiments it appears that the passive films produced without anodic or cathodic treatment were superior to those produced with either treatment. The film produced in nitric acid suffered a much sharper initial decrease in potential than did the chromic acid film. However, after 300 hr the film produced in nitric acid still had a value of +200 mv vs. saturated calomel electrode, whereas the film produced in chromic acid showed a potential of only +80 mv. The film produced by the nitric acid was more resistant to chloride attack than was the film produced by the chromic acid. If resistance to chloride attack is taken as a criterion of the protective character of a film, then the film produced by the nitric acid appears superior to the film produced by the chromic acid.

October 1951

YIE 247

DECLASSIFIED

TECHNICAL NOTES

The Measurement of the Solubility of Fission-product Sulfates at High Temperatures and Pressures

By M. H. LIETZKE
Oak Ridge National Laboratory

Report CF-51-10-142

INTRODUCTION

During the operation of an aqueous homogeneous reactor the fission products will grow into the reactor solution. Eventually the solubility products of some of the fission-product salts may be exceeded, resulting in the precipitation of solid material. The amount of precipitate may be quite significant, especially in the operation of homogeneous reactors of high power ratings, and may have to be considered both during the operation of the reactor and in the solution-decontamination process. Hence it is of interest to determine the solubilities of some of the fission-product salts under the conditions existing in a reactor. Since the homogeneous reactor under construction (the Homogeneous Reactor Experiment) will operate at high temperature and pressure and use a uranyl sulfate solution, it is of interest to determine the solubilities of some of the fission-product sulfates at elevated temperatures and pressures, both in water and in a uranyl sulfate solution of reactor concentration. In the work described here the solubilities of the sulfates of lanthanum, yttrium, cadmium, cesium, and zinc were determined at high temperatures in water, and the solubilities of the sulfates of lanthanum, yttrium, and cadmium were determined at high temperatures in a uranyl sulfate solution containing 30 g of uranium per liter.

EXPERIMENTAL METHODS

With the exception of the determinations below 100°C all solubility measurements described in this report were made by the quartz-tube method described by A. Benrath.[1,2] The quartz-tube method depends upon the visual observation of the appearance or disappearance of crystals in synthetic mixtures of known concentration. Stock solutions of the salts were prepared, and the more dilute solutions were obtained by diluting the stock solution. Spot-check analyses were made of some of the various dilutions, and good agreement between the observed and calculated concentrations was obtained in all cases. In the case of cesium sulfate, which showed a positive temperature coefficient of solubility, the water and crystals were weighed directly into the quartz tubes for each determination.

In place of the 2- to 3-mm tubes used in most of the previous work, 8-mm quartz tubes were employed. These tubes did not permit as high temperatures to be reached as were reached with the 3-mm tubes, but they made the observation of the solution and crystals easier. The tubes were heated in aluminum block furnaces which were mounted on motor-driven rockers so that thorough mixing of the solution and crystals could be accomplished. The temperature was measured by an iron-constantan thermocouple, placed directly above the quartz

714 248
DECLASSIFIED

tube in the furnace, and was recorded on a calibrated Brown recording potentiometer. No significant difference was observed between the temperature recorded by a thermocouple placed within the tube and one placed just above the tube; consequently, no correction was necessary.

The lowest solubility measured was limited in each case by the ability to notice the first appearance of crystals in the tube. In some cases the crystals were visible in much more dilute solutions than in others. For example, the measurement of the solubility of lanthanum sulfate in uranyl sulfate solution could be extended to 0.04 per cent lanthanum sulfate, whereas the cadmium and zinc sulfate limits were much higher (2 to 3 per cent). In all cases the measurements were extended to as dilute solutions as possible.

EXPERIMENTAL RESULTS

Lanthanum Sulfate

The solubility of lanthanum sulfate in water and in a uranyl sulfate solution containing 30 g of uranium per liter is shown in Table 1 and Fig. 1. Data at the lower temperatures from Seidell[3] are plotted on the same graph as indicated.

In both cases the solubility of lanthanum sulfate shows a negative temperature coefficient. Since the lanthanum sulfate solutions all showed a strong tendency to supersaturate, it was necessary to heat them from 50 to 70°C above the equilibrium solubility temperature before crystals appeared. The temperatures given in Table 1 represent the points at which the last crystals redissolved upon slow cooling. The lanthanum sulfate crystals did not adhere to the sides of the tube.

Several of the solutions were heated to 300°C as a check on the possible existence of double solubility points at a given concentration. No such points were observed. When the 0.31 per cent solution was held at 260°C for 48 hr, there was no noticeable change either in the amount or in the type of crystals in the tube. The crystals redissolved easily at the expected temperature when the solution was cooled. Hence it appears that lanthanum sulfate is stable at the temperatures investigated. As a check on the stability of the lanthanum sulfate–uranyl sulfate system in water at high temperatures, the tube containing the 0.87 per cent lanthanum sulfate solution and 30 g of uranium per liter as uranyl sulfate was maintained at 250°C for 72 hr. There appeared to be no change either in the amount or in the form of the lanthanum sulfate crystals in

Table 1 — Lanthanum Sulfate Solubility

In water		In uranyl sulfate solution*	
Temp., °C	$La_2(SO_4)_3$, %	Temp., °C	$La_2(SO_4)_3$, %
26	2.04	97	2.04
108	0.61	105	1.74
113	0.46	120	0.87
115	0.27	145	0.29
117	0.31	169	0.15
		199	0.083
		215	0.042

*Solution contained 30 g of uranium per liter.

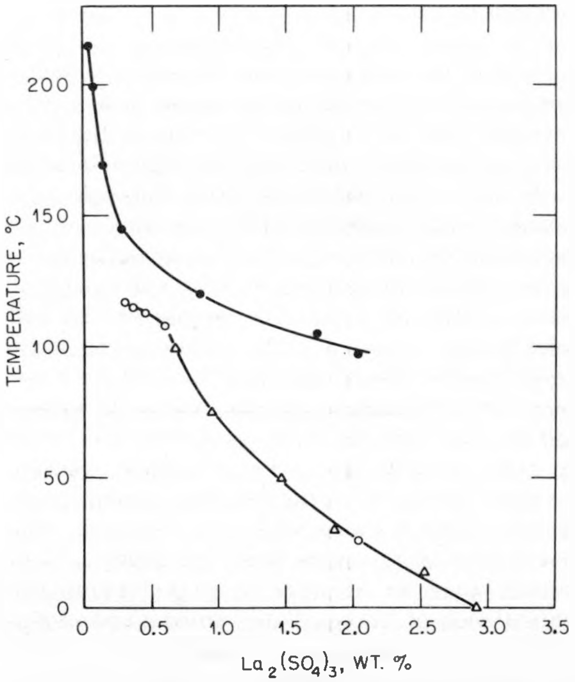


Fig. 1—Solubility curves of lanthanum sulfate. ●, solubility of $La_2(SO_4)_3$ in UO_2SO_4 solution containing 30 g of uranium per liter. ○, solubility of $La_2(SO_4)_3$ in water (Lietzke). △, solubility of $La_2(SO_4)_3$ in water (Seidell).

DECLASSIFIED

the tube. When the tube was cooled, the crystals redissolved at the expected temperature. The lanthanum sulfate–uranyl sulfate–water system therefore seemed to be stable at 250°C. The increased solubility of lanthanum sulfate in uranyl sulfate solution is probably due to strong sulfate complexing by the uranyl sulfate.

Cadmium Sulfate

The solubility of cadmium sulfate in water and in a uranyl sulfate solution containing 30 g of uranium per liter was determined over a wide range of concentrations. Table 2 and Fig. 2 show the results obtained. Data obtained by A. Benrath[1] are plotted on the same graph as indicated. Cadmium sulfate like lanthanum sulfate shows a negative temperature coefficient of solubility, and the presence of uranyl sulfate in the solution increases the solubility of cadmium sulfate at a given temperature. The cadmium sulfate solutions also showed a tendency to supersaturate, hence the temperatures given represent the points at which the last crystals redissolved as the solutions were cooled. The crystals obtained at the higher temperatures, e.g., in the 3 per cent solution, adhered to the walls of the tube, but the crystals from the more concentrated solutions were nonadherent. No double solubility points were found below 300°C at any given concentration. The cadmium sulfate–uranyl sulfate–water system did not appear to be as stable as the lanthanum sulfate–uranyl sulfate–water system. When the 2.8 per cent cadmium sulfate solution containing uranyl sulfate was held for 24 hr at 230°C or for 1 hr at 240°C (below the point at which crystals normally appeared in the solution), a brownish-orange precipitate appeared in the tube. The precipitate redissolved when the solution was cooled. Analysis revealed that the precipitate did not contain any uranium. When the brownish crystals were dissolved in dilute sulfuric acid, a colorless solution resulted. When sodium hydroxide was added to the solution, a white precipitate of cadmium hydroxide was obtained. It appears that the precipitate may have been cadmium oxide.

Table 2—Cadmium Sulfate Solubility

In water		In uranyl sulfate solution*	
Temp., °C	$CdSO_4$, %	Temp., °C	$CdSO_4$, %
124	29.6	175	28.5
160	14.8	200	14.2
182	7.4	219	7.1
190	3.0	251	2.8

*Solution contained 30 g of uranium per liter.

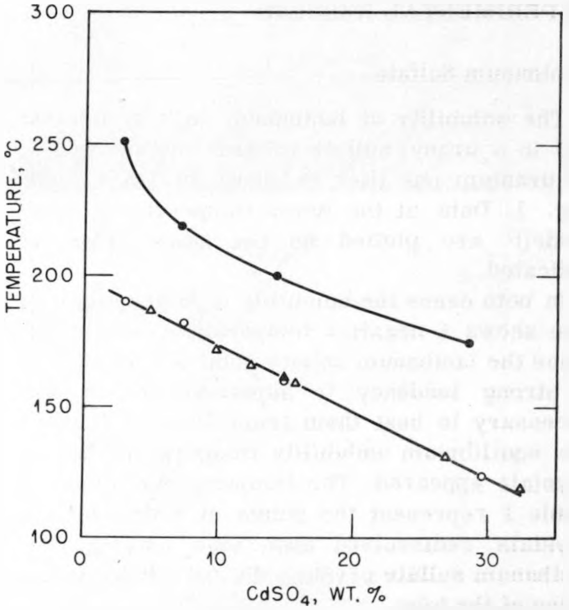


Fig. 2—Solubility curves of cadmium sulfate. ●, solubility of $CdSO_4$ in UO_2SO_4 solution containing 30 g of uranium per liter. ○, solubility of $CdSO_4$ in water (Lietzke). △, solubility of $CdSO_4$ in water (Benrath).

Zinc Sulfate

The solubility of zinc sulfate in water also decreased as the temperature increased. The data obtained are shown in Table 3 and in Fig. 3. Data obtained by Benrath[2] are plotted on the same graph as indicated. The zinc sulfate solutions, unlike the lanthanum sulfate and cadmium sulfate solutions, did not exhibit the strong tendency to supersaturate. No double solubility points at a given concentration were found below 300°C. The crystals of zinc sulfate that appeared adhered to the walls of the tube. Occasionally the zinc sulfate solutions showed very peculiar behavior. For example, when the 2.1

DECLASSIFIED

per cent solution was heated for the very first time, nonadherent crystals appeared in the solution at 225°C. The crystals redissolved on cooling. When the solution was heated again no crystals appeared at 225°C, but the normal adherent crystals were observed at 257°C. The nonadherent crystals could not be produced in the tube again upon several subsequent heatings. This phenomenon was also observed in the 5.1 per cent and in the 11.3 per cent solutions. No explanation is given for this behavior, although the points may indicate an extension of the lower half of the zinc sulfate solubility curve. The 2.1 per cent zinc sulfate solution contained 0.39 mg of silica per milliliter after three heatings to 260°C, while a similar solution that had been heated only once contained only 0.03 mg of silica per milliliter.

Table 3—Solubility of Zinc Sulfate in Water

Temp., °C	$ZnSO_4$, %
178	34.0
203	25.5
219	22.7
238	17.0
248	11.3
253	8.5
255	5.1
257	2.1

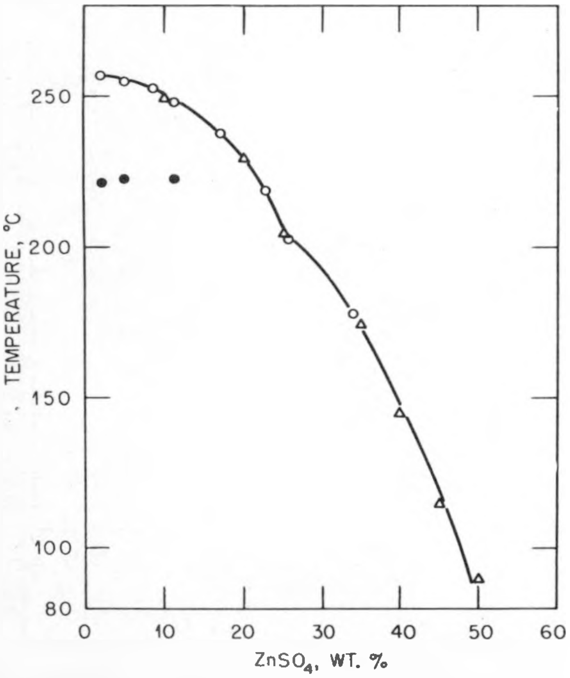


Fig. 3—Solubility curves of zinc sulfate. ○, solubility of $ZnSO_4$ in water (Lietzke). △, solubility of $ZnSO_4$ in water (Benrath). ●, unexplained points.

When the 11.3 per cent zinc sulfate solution was held at 250°C (2 degrees above the point at which crystals appeared in the tube) for 24 hr, a very large amount of crystalline material was deposited in the tube. X-ray analysis of these crystals showed them to be a mixture of $ZnSO_4$ and $ZnSO_4 \cdot H_2O$, which seems to preclude a hydrolytic reaction as the cause of the increased number of crystals. When the 17.0 per cent zinc sulfate solution was held overnight at 210°C (28 degrees below the point at which crystals normally appear), crystals appeared in the solution. These crystals redissolved readily when the solution was cooled, and their composition was not determined.

Cesium Sulfate

The solubility of cesium sulfate in water was determined over a wide range of temperatures. Table 4 and Fig. 4 show the results obtained.

Throughout the range investigated the solubility of cesium sulfate showed a positive temperature coefficient. No crystals reappeared in any of the solutions when they were heated to approximately 310°C (the upper limit for the 8-mm quartz tubes used). The cesium sulfate solutions showed no tendency to supersaturate. In all cases at the elevated temperatures the crystals dissolved and reappeared at exactly the same temperature. The point at 23°C was obtained merely by stirring excess cesium sulfate crystals with water in a beaker. No attempt was made to thermostat the solution, and an ordinary mercury thermometer was used to measure the temperature. The agreement was satisfactory to indicate the correctness of the values in Seidell.[3]

Yttrium Sulfate

The solubility of yttrium sulfate in water and in a uranyl sulfate solution containing 30 g of uranium per liter is shown in Table 5 and Fig. 5.

DECLASSIFIED

In both cases the solubility of yttrium sulfate shows a negative temperature coefficient. Since the yttrium sulfate solutions all showed a strong tendency to supersaturate, it was necessary to heat them from 50 to 70°C above the equilibrium solubility temperature before crystals appeared. The temperatures given in Table 5 represent the points at which the last crystals redissolved upon slow cooling. The yttrium sulfate crystals did not adhere to the sides of the tubes. Just as in the case of lanthanum sulfate no double solubility points were observed at any given concentration below 300°C. Also, the yttrium sulfate–uranyl sulfate–water system seemed to be stable at 250°C.

Table 4—Cesium Sulfate Solubility in Water

Temp., °C	Cs_2SO_4, %
23	63.5
175	71.8
211	73.5
270	75.0
292	75.5

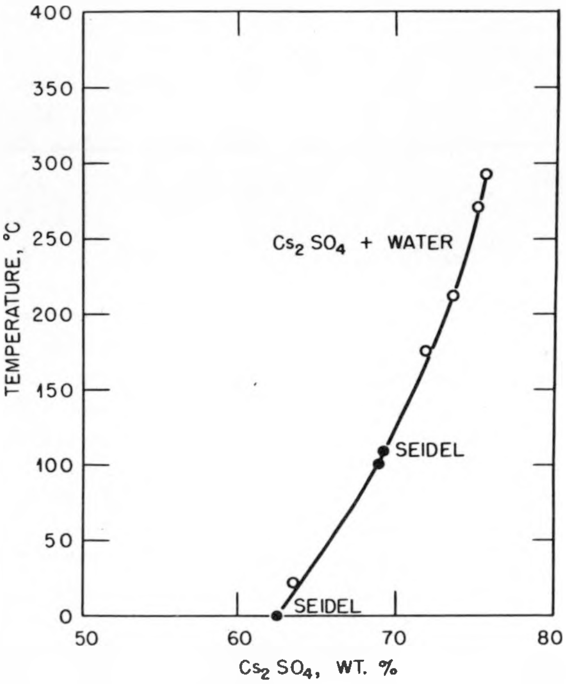


Fig. 4—Cesium sulfate solubility curve.

Table 5—Yttrium Sulfate Solubility

In water		In uranyl sulfate solution*	
Temp., °C	$Y_2(SO_4)_3$, %	Temp., °C	$Y_2(SO_4)_3$, %
108	4.76	153	4.47
150	2.38	162	2.23
155	1.59	189	0.81
160	1.19	229	0.22
161	0.95		
163	0.64		
176	0.48		
186	0.23		
195	0.12		

*The solution contained 30 g of uranium per liter.

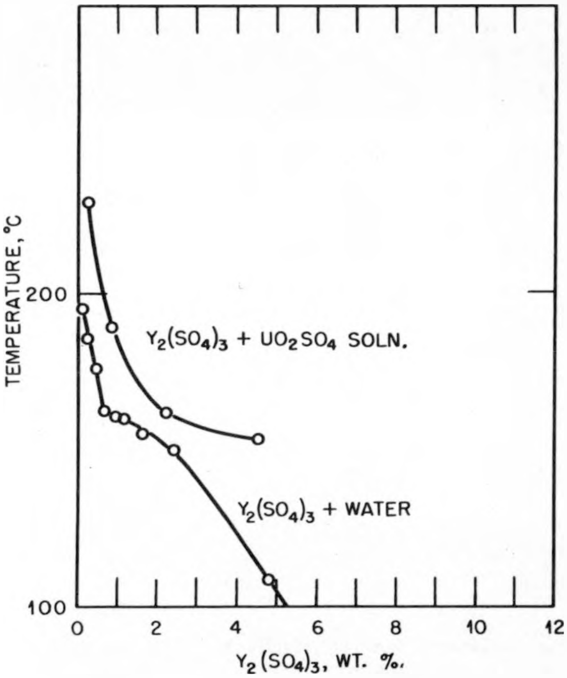


Fig. 5—Yttrium sulfate solubility curves.

CONCLUSION

With the exception of cesium sulfate all the salts investigated showed a negative temperature

DECLASSIFIED

coefficient of solubility both in water and in uranyl sulfate solution. It is possible that at higher temperatures cesium sulfate might behave like sodium and potassium sulfates[3] and show a sudden decrease in solubility. The formation of a sulfate complex of the type $[UO_2(SO_4)_2]^{--}$ may account for the increased solubility of the various sulfates in uranyl sulfate solution at a given temperature. This complex is known to exist at room temperature in sulfate solutions.

Because of the small amount of material used in the synthetic method and because of the difficulty (if not impossibility) of sampling, the solid phase in equilibrium with the solution at a given temperature was not identified.

REFERENCES

1. A. Benrath, Z. anorg. u. allgem. Chem., 231: 285 (1937).
2. A. Benrath, Z. anorg. u. allgem. Chem., 247: 147 (1941).
3. Atherton Seidell, "Solubilities of Inorganic and Metal Organic Compounds," Vol. 1, p. 894, D. van Nostrand Co., Inc., New York, 1940.

October 1951

TECHNICAL NOTES

Notes on Commercial Carbon and Graphite

By J. A. SLYH

Battelle Memorial Institute

Report TID-5046

Among the many basic materials of construction vital to the industrial world, carbon and graphite parts are very important. The peculiar physical and chemical characteristics of the material enable the products to function in roles for which no other material is equally suitable. The various industrial applications include rotating and stationary electrical contacts, electrodes for conducting electrical or thermal energy into areas of utility, and corrosion-resistant materials of construction for the chemical and metallurgical processing industries. With modification, the material may serve as a friction material or a lubricating material in various types of clutch, bearing, and seal applications.

Fabricated carbon is a typical ceramic product, being made of a filler and a binder, shaped, and heat-treated to impart permanency. Prominent among the raw materials that are employed as fillers are petroleum coke, coal, natural graphite, and gas or petroleum blacks. Binders may be any hydrocarbonaceous material which destructively distils leaving carbon residue. Phenol formaldehydes, furfurals, starches, sugars, lignocelluloses, and petroleum and coal asphalts or tars are typical examples. Owing to economic considerations, the latter two are used almost exclusively.

The filler and binder are intimately mixed at a temperature suitable for fluidization of the binder, the resultant mass is formed to shape by molding or extrusion, and the shapes then are baked at 800 to 1500°C to set the binder carbon. Subsequent processing, depending on the ultimate use, may include impregnation with

Table 1 — Properties of Graphites Manufactured by the International Graphite & Electrode Corp.*

Product dimensions, in.	Grade	Texture†	Machine-ability	Transverse strength, psi	Electrical resistivity, ohm-in.	Apparent density, g/cm^3	Maximum ash content, %	Coefficient‡ of thermal expansion, 10^{-7}/°C
9–12 dia. × 72	3383	FG	Good	1500	0.00025–0.00040	1.50–1.65	1.5	23 L
14 dia. × 72	3383	FG	Good	1500	0.00025–0.00040	1.50–1.65	1.5	21 L
16–20 dia. × 60	3383	FG	Good	1500	0.00025–0.00040	1.50–1.65	1.5	19 L
3, 4, 5 dia. × 48	3474	VF		1200	0.00025–0.00045	1.50–1.65	1.5	28 L
6, 7, 8 dia. × 72	3474	VF		1200	0.00025–0.00045	1.50–1.65	1.5	40 T
20 dia. × 60	3474N	F		1500	0.00025–0.00040	1.50–1.65	1.5	
16 × 16 × 74	3474N	F		1500	0.00025–0.00040	1.50–1.65	1.5	
20 dia. × 60	5785	F		1500	0.00025–0.00043	1.60–1.75	1.5	

*These graphites are all manufactured by the extrusion process from petroleum coke, coal-tar pitch, and process oil.
†Abbreviations used are F, fine; FG, fine grain; and VF, very fine.
‡L, longitudinal; T, transverse.

DECLASSIFIED

Table 2 — Properties of Commercial Grades of Carbon and Graphite Manufactured by the National Carbon Division, Union Carbide & Carbon Corp.

Grade	Raw materials; processing operations*	Max. size, in.	Texture†	Structural Flaws	Machineability‡		Transverse strength, psi	Electrical resistivity, ohm-in.	Apparent density, g/cm³	Ash content, %§
					Tool	Grind				
K	Cl, p; extd, gb	40 dia.	C	Some	D	M	1000	0.002	1.61	9.0
CB4	Cl, p; extd, gb	40 dia.	C	Some	D	M	1000	0.002	1.58	7.0
GA	Ck, p; extd, gb	20 dia.	MC	Some	D	M	2500	0.0016	1.57	2.0
MP1	Ck, p; mld, gb	8 × 6 × 4	M	Slight	D	M	3000	0.0016	1.63	2.0
AOH	Lpb, p; mld, impg, grd	6 × 5 × 2½	VF	None	M	G	3500	0.002	1.65	0.1
ATY	Lpb, p; mld, gb	6 × 5 × 2½	VF	None	D	M	4500	0.002	1.50	0.5
ARK	Lpb, p; mld, impg, grd	6 × 5 × 2½	VF	None	M	G	3500	0.002	1.65	0.1
AGR	Ck, p; extd, grd	30 dia.	MC	Some	G	E	1500	0.0004	1.55	0.5
AGX	Ck, p; extd, impg, grd	20 dia.	MC	Some	G	E	2500	0.0004	1.65	0.5
CS	Ck, p; extd, impg, grd	24 dia.	M	Slight	G	E	2500	0.0004	1.65	0.2
ATL	Ck, p; extd, impg, grd	30 dia.	M	Slight	G	E	2500	0.0004	1.65	0.2
ATZ	Ck, p; extd, impg, grd	8 dia.	VF	None	G	E	3500	0.0004	1.65	0.2
AUF	Ck, p; extd, impg, grd	8 dia.	VF	None	E	E	3500	0.0004	1.65	0.06
C18	Ck, p; mld, grd	24 × 20 × 6	F	None	G	E	3500	0.0004	1.57	0.2
ATJ	Ck, p; mld, impg, grd	24 × 20 × 12	VF	None	G	E	4000	0.0004	1.75	0.2
AUC	Ck, p; extd, impg, grd	16 dia.	F	Slight	E	E	2500	0.0004	1.70	0.06
AWC	Ck, p; mld, impg, grd	6 × 5 × 2½	VF	None	E	E	4000	0.0004	1.65	0.06
AWG	Ck, p; mld, impg, grd	24 × 20 × 12	VF	None	E	E	3500	0.0004	1.75	0.06
AGOT-W¶	Ck, p; extd, impg, grd		F	None	E	E	2500	0.0004	1.60	0.06
AGOT-KS¶	Ck, p; extd, impg, grd		F	None	E	E	2500	0.0004	1.70	0.06
GBF	Ck, p; extd, impg, grd		F	None	E	E	2500	0.0004	1.65	0.005

*Abbreviations used are (1) raw materials: ck, coke; cl, coal; lpb, lampblack; and p, pitch and (2) processing operations: mld, molded; extd, extruded; impg, impregnated; gb, gas baked; and grd, graphitized.

†Abbreviations used are C, coarse; MC, medium coarse; M, medium; F, fine; and VF, very fine.

‡Abbreviations used are D, difficult; M, medium; G, good; and E, excellent.

§The analysis of the ash for the coal electrodes, grades K and CB4, is that of coal ash. The analysis of the ash of grades GA and MP1 is that of metallurgical coke. The analysis of the ash of those grades having an ash content in the range of 0.1 to 0.5% is as follows: V_2O_5 = 9 to 40%, SiO_2 = 12 to 35%, Fe_2O_3 = 16 to 30%, CaO = 14 to 26%, TiO_2 = 2 to 5%, sulfur = 0.005 to 0.10%, boron = 1 to 2 ppm. The analysis of the ash of those grades having an ash content of 0.06% is as follows: calcium = 26%, vanadium = 30%, iron = 30%, titanium = 6%, silicon = 8%. Partial chemical analysis of the ash of grade GBF is as follows: boron = 0.1 ppm, calcium = 6 ppm, iron = 10 ppm, vanadium = 5 ppm.

¶Grade AGOT is manufactured only for the AEC and is not considered a commercial stock item. The characteristics quoted for this grade and for grade GBF were obtained from AEC Report BMI-T-35. This report also contains certain characteristics of these grades peculiar to AEC requirements.

Table 3—Properties of Carbon and Graphite Products Manufactured by the Great Lakes Carbon Corp.

Product*	Grade	Transverse strength,† psi	Electrical resistivity,† ohm-in.	Apparent density, g/cm^3	Thermal conductivity, Btu/sq ft/ft/hr/°F	Coefficient of thermal expansion,† 10^{-7}/°F	Tensile strength,† psi	Modulus of elasticity,† 10^5 psi
Graphite electrodes								
3 – 5⅛ dia.	HC	2850	0.00033	1.65	85	15	1000	12
6 – 12 dia.	HC	2000	0.00035	1.56	70	13	625	9.0
14 dia.	HC	1725	0.00035	1.55	70	11	625	8.5
16 – 18 dia.	HC	1510	0.00035	1.55	65	10.5	600	8.3
20 dia.	HC	1100	0.00035	1.54	65	10	575	7.0
24 – 30 dia.	HC	1050	0.00038	1.53	65	10	525	7.0
Graphite blocks								
4 × 4 cross section	HPC	2800	0.00032	1.67	85	13	1075	12
8 × 8 cross section	HPC	2800	0.00033	1.68	85	13	1050	12
16 × 16 cross section	HPC	2520	0.00034	1.69	80	12	1000	11
24 × 30 cross section	HPC	2310	0.00034	1.68	80	12	950	10
Graphite blocks								
4 × 4 cross section	HC	1925	0.00035	1.56	70	12	725	9.2
8 × 8 cross section	HC	1850	0.00035	1.56	70	12	680	8.8
16 × 16 cross section	HC	1710	0.00037	1.57	65	11	625	8.3
24 × 30 cross section	HC	1615	0.00037	1.57	65	11	600	8.0
Carbon electrodes								
8 – 10 dia.	A	1390	0.0011	1.59	9	16		7.0
12 – 17 dia.	A	1200	0.0012	1.57	9	16		6.8
20 – 24 dia.	A	1050	0.0014	1.58	9	15		6.6
30 – 35 dia.	A	910	0.0016	1.57	9	15		6.6
24 × 30 cross section	A	890	0.0016	1.57	9	15		6.6
Carbon brick	BC	2910	0.0019	1.55	3	17	1050	12
Graphite mold stock	HLM	3025	0.00035	1.67–1.70	85	13	1000	12
Graphite anodes	HL	1920	0.00035	1.56	75	11.5	700	11
Up to 2 × 9 cross section	HPL	3050	0.00033	1.66	85	13	1050	13

*Dimensions given in inches.

†Measurements obtained on specimens prepared with their axes parallel to the direction of extrusion.

liquid hydrocarbon, or metal, and/or reheating. Reheating temperatures depend on the type of impregnant. Usually, when no metals are involved, the reheat temperature will be in the range of 2300 to 3000°C, and the resultant product is called "artificial graphite," or graphite.

Carbon or graphite shapes are employed in large quantities in production and experimental work for the Atomic Energy Commission. Prominent applications include the use of graphite as moderator and reflector components for nuclear reactors; also, considerable study is being made of the possible use of graphite as a material of construction for fuel elements and crucibles. Other applications arise for speculation frequently in considering the design of apparatus and equipment. Typical properties of graphites manufactured by International Graphite & Electrode Corp. are given in Table 1. To serve as a single reference, some of the more common physical characteristics, and the raw materials and processing operations employed in the fabrication, of many of the commercial grades of the National Carbon Division of the Union Carbide & Carbon Corp. are presented in Table 2. Typical properties of the carbon and graphite products of the Great Lakes Carbon Corp. are given in Table 3.

We acknowledge the aid of B. W. Gamson of the Great Lakes Carbon Corp., L. C. Werking and W. A. Steiner of the National Carbon Division, and G. J. Goepfert of the International Graphite & Electrode Corp. in the preparation and release of these data.

October 1951

DECLASSIFIED

LETTERS TO THE EDITORS

To the Editors:

G. L. Weil stated, in a recent review [Reactor Sci. Technol., 1: 7(1951)], that in the case of a converter a few per cent gain in conversion ratio is relatively unimportant, whereas a few per cent gain in breeding ratio for a breeder may make a large difference in the ultimate supply of fissionable material. In the case of the conversion of U^{235} to U^{233} or to plutonium this is true because of the relative paucity of U^{235}. However, if the conversion of plutonium to U^{233} is considered (or the reverse conversion), the situation is entirely analogous to the breeding problem. There may even be some worth-while technological advantages in conducting what is essentially a breeding process by converter reactors.

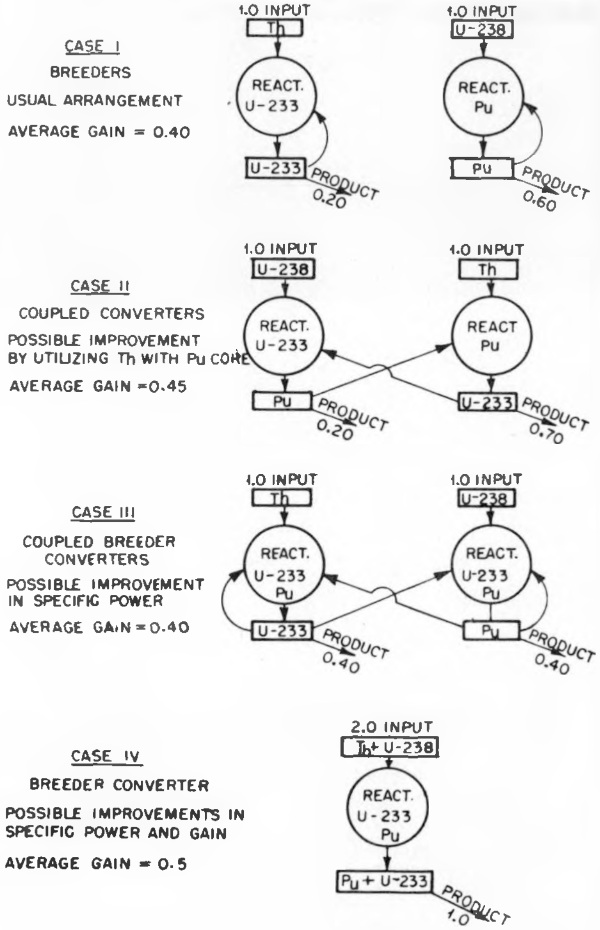
The only obvious advantage seems to be the additional flexibility in the type of product output obtained by considering converters as well as breeders. In the diagram are shown the two breeder arrangements and various alternate schemes. Case I represents the usual breeder arrangement with assumed breeding gains of 0.2 for the thorium-U^{233} cycle and 0.6 for the U^{238}-plutonium cycle.

Case II represents two coupled converters with the plutonium core fed thorium and the U^{233} core fed U^{238}. Each converter maintains the core of the other. The element of flexibility now enters in that the relative production of U^{233} and plutonium is 0.6 to 0.2, whereas it had been the reverse with breeders.

There is a possible secondary advantage. In order to obtain a high breeding gain, the plutonium core must operate with a rather fast neutron spectrum. Thorium has a larger resonance absorption integral than U^{238} and may be more efficient in absorbing the fast spectrum neutrons. This is indicated by changing the output from 0.6 to 0.7 on the plutonium-core reactor.

In case III, mixed-core coupled breeder-converters are considered, with one fed thorium and the other fed U^{238}. A possible advantage of this scheme may be operation at a higher specific power than is possible with good gain with a straight plutonium core. The stringent limitations on neutron spectrum may be relaxed when U^{233} is present to fission in the lower energy range where the plutonium radiative capture cross section is large. With the limitation on spectrum removed, more coolant may be used and a higher specific power may be obtained.

In case IV, the mixed-core mixed-feed breeder-converter is indicated. This arrangement has the possible advantages of high specific power (mixed core) and improved breeding gain by optimum absorption utilizing the mixed feed. This is indicated by the product output of 1.0.



DECLASSIFIED

The only certain advantage of the breeder-converter arrangements over straight breeder systems is the greater flexibility in type of product. The realization of the other possible advantages will depend upon the details of the U^{233} fission and capture cross sections, and this knowledge is lacking. The breeding gain of the mixed schemes will be lower than for the straight plutonium-U^{238} cycle because the lower gain U^{233}-thorium is averaged in. However, if U^{233} production were to be emphasized, case II would seem to be superior to case I.

M. M. Mills

Atomic Energy Research Department
North American Aviation, Inc.
Downey, California

Supplementary Reading List

Article by B. H. Alexander et al., "The Application of Powder Metallurgy to Problems Involving Beryllium, Zirconium, and Uranium."

R. P. Angier and H. H. Hausner, The Development of Uniform Distribution of Uranium in Beryllium by Means of Powder Metallurgy II, Report SEP-14, May 26, 1949.

R. P. Angier and H. H. Hausner, An Investigation into the Powder Metallurgy Processing of Zirconium Dihydride and Zirconium Powders Prepared from Zirconium Crystal Bar, Report NYO-1127, Apr. 10, 1950.

R. P. Angier and H. H. Hausner, The Preparation of Zirconium Hydride and Zirconium Metal Powders and Observations in the Zirconium-Hydrogen System, Report SEP-28, Dec. 28, 1949.

F. E. Croxton, Bibliography on Powder Metallurgy with Emphasis on Porous Metals, Reports AECD-2763 and K-193, Apr. 2, 1948.

H. H. Hausner and N. P. Pinto, The Powder Metallurgy of Beryllium, Reports AECD-2869 and SEP-12, Mar. 24, 1949.

H. R. Hoge and B. Lustman, The Consolidation of Zirconium at Sub-fusion Temperatures, Report WAPD-12, Apr. 17, 1950.

B. Kopelman, The Process of Pulse Sintering, Report SEP-33, Dec. 22, 1949.

N. P. Pinto, The Production of Uranium Powder, Report SEP-16, May 26, 1949.

N. P. Pinto and H. H. Hausner, Hot Pressing of Uranium, Report NYO-1129, July 8, 1950.

N. P. Pinto and H. H. Hausner, The Production of Uranium Bars by Powder Metallurgy, Report SEP-18.

H. A. Saller, J. R. Keller, and N. S. Eddy, Control of Particle Size in Aluminum-Uranium Alloys, Report BMI-T-16, Nov. 15, 1949.

A. U. Seybolt, R. M. Linsmayer, and J. P. Frondsen, A Process for Hot Pressing Beryllium Powder, Report AECD-2679, Aug. 18, 1949.

W. W. Wellborn and J. R. Armstrong, Metallic Filters: Their Fabrication and Uses, Report AECU-838, June 28, 1950.

Article by Lane "Some Long-range Aspects of Homogeneous Reactors."

F. E. Croxton, List of References on Homogeneous Reactors, Report TID-299, Feb. 27, 1950.

Article by J. H. Arnold, M. Benedict et al., "Survey of Processes for Separation of the Products of Nuclear Reactors."

L. A. Barry, G. H. Montillon, and R. Van Winkle, Fluorination of Uranium Pile Slugs with Elemental Fluorine, Report K-548, Dec. 30, 1949.

J. C. Barton and R. H. Rainey, Laboratory Development of the UAP Process, Report K-621, Aug. 4, 1950.
Chemical Separations Processes: Session X, General Information Meeting, Oct. 24, 25, and 26, 1949, Oak Ridge, Tennessee. Report TID-276.

J. M. Fletcher and K. D. B. Johnson, The Butex Process for the Separation of Plutonium: Review of Position at April 1950, Reports AERE-C/R-548 and HDS-109, June 1950.

J. M. Frame, Summary Outline of Redox Flow Sheet Process Chemistry, Report HW-7819, Oct. 17, 1947.

J. S. McLaren, H. S. Clinton, J. J. Finley, and H. Goode, The Electrochemical Processing of Uranium Slugs: Preliminary Studies on Metal Dissolution, Plutonium Separation, and Uranium Recovery, Report K-601, Sept. 8, 1950.

R. C. Olson, J. H. Pashley, D. H. Stewart, and J. L. Waters, An Evaluation of the TBP Process and a Comparison with the UAP Process, Report K-540, Dec. 14, 1949.

L. C. Perry, J. V. P. Torrey, and J. P. Cooke, Feasibility of the Redox Solvent Extraction Process as a Method for Separation and Determination of Plutonium and Uranium. A Process Evaluation and Cost Study. Reports A-3921 and HW-7-3462, Mar. 1, 1947.

S. Peterson and H. R. Hoekstra, A Study of the Bismuth Phosphate Extraction Step at Production-plant Concentrations of Plutonium, Report CN-3669, Nov. 6, 1946.

T. C. Runion and C. V. Ellison, Application of the Purex Process to ORNL Metal Waste Recovery, Report ORNL-743, Aug. 24, 1950.

G. I. Staber, Detailed Project Status Report: Kellex Chelation Process, Job 11, Report KLX-56, Sept. 2, 1949.

DECLASSIFIED

SUPPLEMENTARY READING LIST

Article by A. H. Barnes et. al., The Exponential Experiments at Argonne National Laboratory.

Chernick, J., I. Kaplan, J. Kunstadter, V. Sailor, and C. Williams, An Experimental and Theoretical Study of the Subcritical BNL Reactor, Report BNL-60, June 15, 1950.

Egelstaff, P., The Exponential Experiment on the Harwell Pile, Report AERE-N/R-250, Sept. 23, 1948.

Glasstone, S., and M. C. Edlund, The Elements of Nuclear Reactor Theory, Parts I, II, and III, Reports TID-384, TID-385, and TID-386, November 1950.

Article by A. M. Gaudin et. al., Lyometallurgy: A New Method of Extracting Uranium from Its Ores.

Bain, W. A., Evaluation of Solvent-leaching Process for Pitchblendes, Report KLX-1210, Jan. 5, 1951.

Solvent Evaluation for Liquid-Liquid Extraction, Closing Report (23-F) Report KLX-1211, Jan. 15, 1951.

Article by S. Siegel, A High-temperature Reactor for Power Breeder Application.

Morphew, A. T., F. E. Croxton, and R. L. Morgan, Selected Classified References on Nuclear Reactors, Report TID-3004, May 10, 1951.

Shannon, R. L., Nuclear Breeding; A Literature Search, Report TID-389(rev.), November 1950.

Article by W. E. Winsche et. al., The Hot Laboratory at Brookhaven National Laboratory.

Blomgran, R. A., and F. Hagemann, Improved Chemistry Cave, Report ANL-4426, Mar. 1, 1950.

Bohlin, N. G., and S. S. Gold, Machine Tool Hoods, Report ANL-4418, Mar. 1, 1950.

FitzPatrick, J. P., N. G. Bohlin, and S. S. Gold, Low-activity Hoods, Reports AECU-617 and ANL-4336, May 20, 1949.

Guest, G. H., and L. G. Cook, Design, Auxiliary Equipment, and Services for a Radiochemical Laboratory, Reports CRHR-368 and NRC-1714, Feb. 14, 1948.

Hawkins, M. B., The Design of Laboratories for the Safe Handling of Radioisotopes; Isotopes Division Circular B-5, Report IDB-5.

Hull, H. L., R. C. Goertz, and K. R. Ferguson, New Hot Laboratories at Argonne, Reports AECD-2990 and ANL-4385, October 1949.

Jealous, A. C., Problems in Planning Facilities for Radiochemical Process Development, Report AECD-2512, February 1949.

Little, A. D., Inc., Final Report on Decontaminable Surfaces for a Low-level Radioactivity Laboratory to the University of Chicago and Argonne National Laboratory, Report ALI-19, Oct. 7, 1949.

McEwen, M., Development of Special Hoods, Report MLM-301, Mar. 24, 1949.

Mackintosh, A. D., The Architectural Approach to Radiochemical Laboratory Design, Reports AECU-210 and ORNL-335, Apr. 13, 1949.

Race, H. H., R. H. Horton, J. P. Howe, J. R. Low, H. H. Zornig, F. A. Vernon, and C. H. Betts, Project SIR; Revised Proposal for the Radioactive Materials at the KAPL, Report KAPL-387, Aug. 3, 1950.

Stewart, P. J., Plant Research with Active Materials, Report AERE-ER-167.

Walters, F. M., Some Considerations Involved in the Design of a Laboratory for Work with Alpha Active Materials, J. Met. Ceram., 4: 58-61, (September 1949).

Watson, C. D., T. H. Handly, and G. A. West, Decontamination and Corrosion Resistance Properties of Selected Laboratory Surfaces, Reports ORNL-732 and AECD-2996, Aug. 29, 1950.

White, G., Jr., Feasibility Report; Kellex "Hot" Laboratory, Job 11, Report KLX-14, Aug. 2, 1948.

Whittlesey, E. and E. Givens, Bibliography; Radiation Protection of Personnel and Radiochemical Laboratories; Their Design and Operation, Report AECU-1020, July 1950.

Zornig, H. H., Survey of Basic Principles Affecting the Design and Operation of Radioactive Materials Laboratories, Report KAPL-384, July 1, 1950.

SUPPLEMENTARY READING LIST

Article by E. P. Blizard and T. A. Welton, "The Shielding of Mobile Reactors (I)."

G. A. Allard, R. W. Lockhart, H. P. Sleeper, and H. E. Stone, Choice of SIR Shield Materials and Preliminary Shield Design Studies, Report KAPL-491, Mar. 31, 1951.

ANP Shielding Board, Report of the ANP Shielding Board. . .for the Aircraft Nuclear Propulsion Program, Report ANP-53, Oct. 16, 1950.

Fairchild Engine & Airplane Corp., NEPA Division, The Theory of an Aircraft Shield, Report NEPA-1660, January 1951.

W. J. McShane and T. P. Evans, Submarine Nuclear Power Plant Shielding, Report WAPD-6, Mar. 1, 1950.

M. Neustadt and E. R. Cohen, Reactor Self-Shielding, Report NAA-SR-112, Apr. 20, 1951.

T. Rockwell III and A. S. Kitzes, Theoretical and Practical Aspects of Shielding, Report ORNL-710, Sept. 29, 1950.

J. M. Ruddy, Gamma Ray Shielding for Engineering Reference, Report AECU-1211, Feb. 15, 1951.

J. J. Taylor, Submarine Thermal Reactor Shield Design, Report WAPD-23, January 1951.

R. Zirkind, Technical Summary of All ORNL Summer Shielding Session (1945), Report ORNL-503, June 19, 1950.

Article by R. O. Bolt, J. G. Carroll, and G. H. Denison, "The Effects of Fission Radiations on Lubricants and Lubrication."

H. E. Voress, The Effects of Radiation on Organic Materials; A List of References on the Subject, Report TID-3016, Oct. 13, 1951.

Article by F. R. Bruce, "A Survey of Homogeneous-reactor Chemical Processing."

F. E. Croxton, Homogeneous and Fluid Fuel Reactors; A List of References on the Subject, Report TID-3007, June 20, 1951.

DECLASSIFIED